



Review

Carbon nanotubes: Solid-phase extraction

Lidia M. Ravelo-Pérez, Antonio V. Herrera-Herrera,
Javier Hernández-Borges*, Miguel Ángel Rodríguez-Delgado**

Departamento de Química Analítica, Nutrición y Bromatología, Facultad de Química, Universidad de La Laguna (ULL), Avenida Astrofísico Francisco Sánchez, s/n, 38206 La Laguna, Tenerife, Spain

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ABSTRACT

Since the first report in 1991, carbon nanotubes (CNTs) have shown great possibilities for a wide variety of processes and applications, which include their use as electrodes, sensors (gas, enzymatic, etc.), nanoprobe, electronic materials, field emitters, etc. The combination of structures, dimensions and topologies has provided physical and chemical attractive properties that are unparalleled by most known materials. Their applications have also reached the Analytical Chemistry field in which CNTs are being used as matrices in matrix assisted laser desorption ionization, stationary phases in either gas chromatography, high performance liquid chromatography or capillary electrochromatography, also as pseudostationary phases in capillary electrophoresis, etc. as well as new solid-phase extraction (SPE) materials. Concerning this last application the number of works has considerably increased in the last five years. This review article pretends to focus on the most important features and different applications of SPE using CNTs (including matrix solid-phase dispersion and solid-phase microextraction) covering articles published since their introduction up to now (September 2009).

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1. Introduction

Nanotechnology is nowadays one of the most important trends in science, perceived as one of the key technologies of the present century. Its applications include the biotechnology and pharmacy fields as well as electronics, scientific tools, industrial manufacturing processes, the introduction of advance materials, etc. In this last aspect, nanotechnology includes the production of novel and re-

volutionary materials of the size of 100 nm or even smaller. Carbon nanotubes (CNTs) are part of these novel materials. Their discovery was a direct consequence of the synthesis of fullerenes, especially the buckminsterfullerene, C₆₀, in 1985 [1,2]. The finding that carbon could form stable, ordered structures different than those of graphite and diamond encouraged scientists to investigate the possible existence of other forms of carbon. In 1990, the research became even more intense when it was found that C₆₀ could be produced in a simple arc-evaporation apparatus (which were available in many laboratories) [3].

In 1991, Sumio Iijima [4] reported the preparation of a new type of finite carbon structures (designated at that time as “helical microtubules of graphitic carbon”) using an arc-discharge evaporation method, very similar to that previously used to synthesized

* Corresponding author. Tel.: +34 922 31 80 12; fax: +34 922 31 80 03.

** Corresponding author. Tel.: +34 922 31 80 46; fax: +34 922 31 80 03.

E-mail addresses: jhborges@ull.es (J. Hernández-Borges), mrguez@ull.es (M.Á. Rodríguez-Delgado).

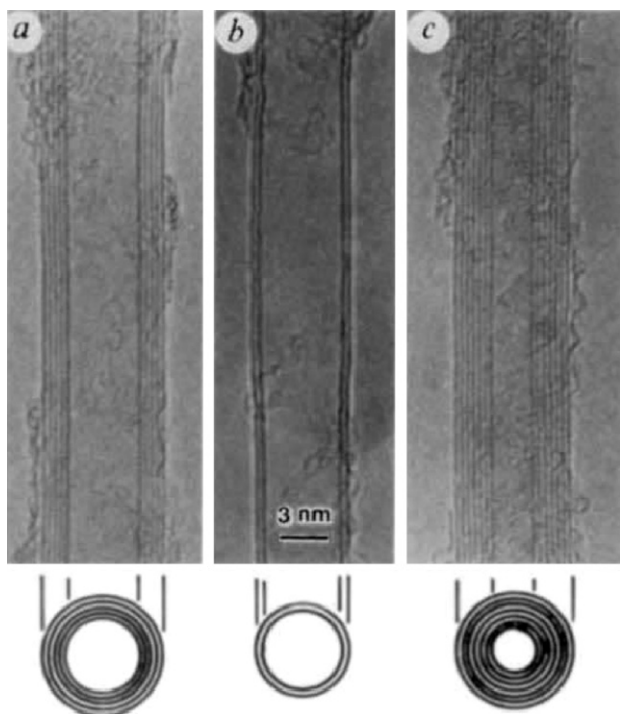


Fig. 1. Electron micrographs of “microtubules of graphitic carbon” obtained in the first report of CNTs [4]. Parallel dark lines correspond to the (002) lattice images of graphite. A cross-section of each tubule is illustrated. (a) Tube consisting of five graphitic sheets, diameter 6.7 nm. (b) Two-sheet tube, diameter 5.5 nm. (c) Seven-sheet tube, diameter 6.5 nm, which has the smallest hollow diameter (2.2 nm). Reprinted from [4] with permission from Nature Publishing Group.

fullerenes. Electron microscopy revealed that these first graphitic carbon needles were made of coaxial graphitic tubes (up to about 50) ranging from 4 to 30 nm diameter, up to 1 μm in length and invariably closed at both ends (Fig. 1 shows the electron micrographs of the microtubules of graphitic carbon obtained in this work). CNTs are therefore molecular-scale tubes of graphitic carbon which can be consequently considered as a graphene sheet in the shape of a cylinder. Their initial designation soon evolved into multi-walled CNTs (MWCNTs) which better reflects their structure. This initial work showed that the engineering of carbon structures of different shapes and bigger than fullerenes was also possible. It should also be remarked that tubular structures like these ones are rarely found in nature, except for some silicate minerals such as chrysotile asbestos [5]. Two years later, Iijima and Ichihashi [6] and Bethune et al. [7] showed that catalytic vapor deposition could be controlled to make single-layer tubular structures of graphene with diameters as small as 1 nm. These structures were later called single-walled CNTs (SWCNTs) and were synthesized in the gas phase by the same route of producing MWCNTs but adding some metal particles, usually iron, copper or nickel, to the carbon electrodes. In general, CNTs have diameters between fractions of nanometers and tens of nanometers and with lengths up to several micrometers. Their ends are normally capped by fullerene-like structures.

Nowadays, it is possible to synthesize CNTs in high quantities with a relatively precise number of layers (although more work needs to be done on this aspect) being at present, arc-discharge [8], laser ablation [9] and chemical vapor deposition [10] the three main employed methods. The main drawback of these methods concerns the purity of the final materials, which inevitably contain impurities of amorphous carbon, fullerenes, carbon nanoparticles and metal catalyst particles. The amount of impurities normally increases with the decrease of CNTs diameter [11–15]. Thus, a num-

ber of purification methods (based on either chemical [16–18] or physical [19–22] procedures or a combination of both) have been skillfully developed to date [11,23,24].

CNTs exhibit single physical and chemical properties that make them potentially useful in many applications like electronics, optics, chemistry, etc. and other fields of materials science, as well as potential uses in architectural fields. SWCNTs, in particular, show more dominant properties originated from their one-dimensionality, which becomes more dominant as its diameter becomes smaller. Another important factor that controls these unique properties comes from a variation of tubule structures that are caused by the rolling up of the graphene sheet into a tube. Taking into account that hybridation of carbon in CNTs is sp^2 (with each atom joined to three neighbors, like in graphite) there are three distinct ways for the molecule to do the rolling, depending upon its direction. The first of them is known as “armchair” and provides metallic character. The second is called “zig-zag”. The terms “armchair” and “zig-zag” refer to the arrangement of hexagons around the circumference. Both of them have a high degree of symmetry and an achiral character. The third class of tube, which is, in practice, the most common, is known as “chiral” and provides a semiconductor character, meaning that it can exist in two mirror-related forms [25].

Based on their structure, CNTs show unique properties [26]: (i) lightness, high tensile strength, extremely high thermal conductivity and stability as well as high resilience, (ii) CNTs undergo non-reversible deformation or plastic deformation when given extremely high tensile strain (due to their hollow structure, CNTs change their shape (buckling) under compressive stress), (iii) electrical properties of CNTs are very different: they can be excellent conductors (with conductivity 1000 times the one of copper) or semiconductors, depending upon the arrangement of the graphene layers [27], (iv) CNTs align themselves into ropes held together by van der Waals forces and can merge together under high pressure, trading some sp^2 bonds to sp^3 and producing very strong wires of nanometric lateral dimension, (v) high insolubility in water which makes them difficult to purify and characterize. However, CNTs can be solubilized in aqueous medium by the addition of chemical modifiers such as surfactants [28,29], end or side-wall functionalization [30] or oxidative treatments [31]. They also show high insolubility in organic solvents only exhibiting a sufficient solubility in a restricted number of them, such as dimethyl acetamide, hexamethylphosphoramide, dimethyl pyrrolidone and dimethyl formamide [32,33], (vi) CNTs are not reactive, but their reactivity can increase due to CNTs can be functionalized by different ways, mainly both covalently and non-covalently [34–38]. Concerning CNTs modifications, boron and nitrogen doping as well as metal-filled CNTs have also been described [30].

Among the current different uses of these advanced materials, CNTs have also found in the analytical chemistry field a new application area, as can be seen in different review articles dealing with this general aspect [26,30,31,35,38]. It is worth mentioning their use for the construction and improvement of electrochemical detectors [39–43] as well as their employment in the fabrication of membranes for filtration purposes (they generally form part of polymeric membranes) [44–49], since it has also been demonstrated that fluids can flow through their cores [50,51]. Chromatographic applications of CNTs have been focused on their use as stationary phases in either GC [52–56] or LC [57] while in CE they have been utilized as pseudostationary phases being part of the BGE [58–63] and also as stationary phases in CEC [64], although a higher number of works are still to come. Another interesting application is also their use as matrices in MALDI which has been studied several times with interesting results [65–70].

The use of CNTs as SPE sorbents for the extraction of both organic and inorganic compounds is also a relatively important field of

application which has especially emerged in the last five years when the number of works has greatly improved. SPE is widely accepted for analyte extraction and preconcentration as an alternative to time consuming and laborious liquid–liquid extraction (LLE) procedures. The key of the problem when applying SPE remains always the method development and the primary decision that must be taken is the selection of the most appropriate sorbent, which depends on the physico-chemical properties of the analytes. In this sense, as previously indicated, CNTs' high surface area, ability to establish π – π interactions, excellent chemical, mechanical and thermal stability, etc. make them very attractive as SPE materials for either non-polar (in the case of non-functionalized CNTs) and polar compounds for which functionalization of the tubes plays a key role in selectivity.

The aim of this work is therefore to provide an updated and critical revision of the most important features and applications of CNTs as new SPE materials (including solid-phase microextraction, SPME) since their discovery in 1991. Emphasis will be placed on the description of the different works that have provided interesting results for their use in this analytical field. This is the first review article that focuses on this specific subject.

2. Applications of carbon nanotubes in solid-phase extraction

From a detailed revision of the current literature it is clear that CNTs present an adequate sorption capacity for the extraction of both organic and inorganic compounds as it will be demonstrated in the following sections. These works have shown that in general it is highly necessary to dry CNTs at least at 80–120 °C for a couple of hours [71–73] prior to their use as SPE sorbents, and depending on the application, they can be reused or not. However, concerning this last aspect, reusability has only been reported few times [74–77]. All these applications have also been developed in laboratory made cartridges (since no commercialized ones are available). Despite this fact, good reproducibility between cartridges has been achieved.

A change in selectivity has also been achieved by covalently functionalizing their surface [78] in a higher scale at their fullerene-like tips which are more reactive than their walls. In this sense, CNTs can be made to react under strong chemical conditions usually incorporating hydroxyl, carboxyl or carbonyl groups onto their side-walls [79]. Reactions of halogenation, hydrogenation, radical addition, nucleophilic addition and cycloaddition have been described [80]. CNTs can also be covalently immobilized onto solid supports such as steel or silica and thus, changes in the geometry of the SPE device can take place. On the other hand, non-covalent side-wall functionalization of CNTs also provides a change in selectivity. In this case, this type of functionalization includes ionic interactions (e.g., dipole–dipole), π – π stacking, hydrogen bonds, electrostatic forces, van der Waals forces, dative bonds and hydrophobic interactions. The combination of two or more similar or different interactions increases the stability and the selectivity of the system.

The following section describes in detail the different applications of CNTs for SPE, including their use in SPME or micro-SPE devices, published since their introduction in 1991.

2.1. Organic analytes

Regarding apolar organic analytes, generally, non-functionalized CNTs highly retain them. In fact, it is very frequent in these applications to use high volumes of eluent solvents. Besides, hexagonal arrays of carbon atoms in grapheme sheets interact strongly with aromatic rings, due probably to van der

Waals interactions [81]. On the contrary, the retention of polar organic analytes is better carried out with functionalized CNTs. Tables 1–3 show the different applications that have appeared in the literature up to now concerning the extraction of organic compounds from different matrices. As it can be seen, CNTs have been successfully used as SPE sorbents for the extraction of different families of pesticides [46,71,72,74,75,82–110], drugs [111–117], phthalate esters [118–120], phenolic compounds [121–129] and others [130–143] prior to their determination by either GC [46,72,74,88,92,96,98,101,102,106–108,111,114,123,124,127,129–131,133,140,141,143], HPLC [71,75,82–87,89–91,93,95,97,99,104,105,109,110,112,116–122,126,128,135–137,139] and even, although in a much lower extent, CE [100,113,115]. In the majority of these works aqueous samples were analyzed and just in several occasions other samples different than waters were studied. It is worth mentioning the direct extraction of fruit juices [98], virgin olive oil [74], milk [133], sewage sludge [46], air [130], urine [113,117,132] and blood [134,142], and also the extraction of soils [96,107,110], garlic [94], pork [111,112,114] and eggs [112], for which a previous solid–liquid extraction procedure is necessary. The following sections describe in detail some of these applications attending to the groups of analytes mostly analyzed.

2.1.1. Pesticides

Regarding the extraction of pesticides, in general SPE has been increasingly used because of its high extraction efficiency, the ease of method development, the lower amount of organic solvents used and the possibilities of automation when compared to classical LLE. Table 1 compiles the specific applications of CNTs sorbents in this sense for which CNTs have shown to outperform many popular solid-phase extractants. As it can be seen in Table 1, most of these works have employed MWCNTs of wide outer diameter (o.d.), mainly of 30–60 nm [71,75,82–85,89–91,99,104] and 40–60 nm [88,95–97,103,106,110] and in lower extent SWCNTs [74,101,105]. As an example of the use of wider MWCNTs, Zhou et al. [89] demonstrated the application of 30–60 nm o.d. MWCNTs as SPE cartridge packing for the extraction of metalaxyl, diethofencarb, myclobutanil, prometryn and tebuconazole in tap, ground, rain and reservoir waters prior to their HPLC–UV determination. Parameters influencing the enrichment (kind and volume of eluent, sample pH, flow rate and sample volume) were optimized by means of a step by step approach, being the optimal conditions 500 mL of sample at pH 7, a flow rate of 11 mL/min and elution with 6 mL of dichloromethane. Under these conditions, LODs and recovery percentages were in the range of 2.99–6.04 ng/L and 79–109%, respectively. According to the obtained results, the method was sensitive, simple, rapid and easy to perform as well as repeatable.

On the other hand, fewer authors have used lower o.d. MWCNTs, i.e., 3–10 nm [93], 5–10 nm [86], 8.6 nm [102,108], 10–15 nm [72,98,100,107] and 10–20 nm [87,109]. Ravelo-Pérez et al. [72] investigated for the first time the use of MWCNTs of 10–15 nm o.d. for the extraction of seven organophosphorus pesticides (ethoprosfos, diazinon, chlorpyrifos-methyl, fenitrothion, malathion, chlorpyrifos and fenamiphos) and one thiazidiazine (buprofezin) from different water samples (mineral, ground and run-off waters) using GC–NPD. Optimum extraction conditions were 40 mg of MWCNTs, 800 mL of sample at pH 6 and 20 mL of dichloromethane as elution solvent. It was found out that these MWCNTs showed excellent extraction efficiency with a high repeatability, selectivity and very low cost. LODs achieved were between 18 and 117 ng/L which were below the maximum residue limits (MRLs) established by the European Union (EU) legislation for these compounds in waters. Moreover, these authors extended the application of this procedure to the direct extraction of the same group of pesticides from apple, grape, orange and pineapple juices [98]. For this purpose, it was necessary to dilute the sample, introduce a washing

Table 1
Applications of CNTs as SPE sorbents for the extraction of pesticides from different samples.

Analyte	Matrix	Method	CNTs characteristics	CNTs amount (mg)	Recovery (%)	LOD	Enrichment factor	Remarks	Reference
Triethylphosphorothioate, thionazin, sulfotep, phorate, disulfoton, methyl parathion and ethyl-parathion	Sewage sludge	GC-MS	MWCNTs: –	6	–	1–7 pg/g	200 (sample volume: 20 mL; eluent volume: 0.1 mL)	μ-SPE. Comparison was made with hollow fiber protected-SPME and HS-SPME (μ-SPE gave lower LODs)	[46]
Atrazine and simazine	River, reservoir, waste and tap water	HPLC-DAD	MWCNTs: o.d.: 30–60 nm	100	58–104	33 and 9.0 ng/L	125 (sample volume: 500 mL; elution volume: 4 mL)	Before use, MWCNTs were dried at 80 °C for 2 h	[71]
Ethoprofos, diazinon, chlorpyrifos-methyl, fenitrothion, malathion, chlorpyrifos, fenamiphos, and buprofezin	Mineral, ground and run-off water	GC-NPD	MWCNTs: o.d.: 10–15 nm, i.d.: 2–6 nm, length: 0.1–10 μm	40	40–119	18–117 ng/L	800 (sample volume: 800 mL; reconstitution volume: 1 mL)	Before use, MWCNTs were dried at 120 °C for 2 h	[72]
Chlortoluron, diuron, atrazine, simazine, terbuthylazin-desethyl, dimethoate, malathion and parathion	Virgin olive oil	GC-MS	MWCNTs: o.d.: 20–30 nm, i.d.: 5–10 nm, length: 0.5–200 μm; SWCNTs: o.d.: 1–2 nm, length: 0.5–2 μm	30	79–105	1.5–3.0 μg/L	60 (sample volume: 3 mL; reconstitution volume: 50 μL)	Study of carboxylated CNTs as SPE sorbents	[74]
Cyanazine, chlorotoluron and chlorbenzuron	Tap, ground, sewage and snow water	HLPC-UV	MWCNTs: o.d.: 30–60 nm	100	88–110	12–34 ng/L	250 (sample volume: 250 mL; reconstitution volume: 1 mL)	Comparison between MWCNTs and C ₁₈ (MWCNTs were at least as effective as C ₁₈ for cymazine and chlorotoluron, but they were more effective for chlorbenzuron)	[75]
Atrazine and simazine	River, reservoir, waste and tap water	HPLC-DAD	MWCNTs: o.d.: 30–60 nm	100	60–105	33 and 9.0 ng/L	125 (sample volume: 500 mL; elution volume: 4 mL)	Before use, MWCNTs were dried at 80 °C for 2 h. Comparison between MWCNTs, activated carbon and C ₁₈ (MWCNTs provided similar recoveries to C ₁₈)	[82]
Nicosulfuron, thifensulfuron-methyl and metsulfuron-methyl	Tap, sea, reservoir and well water	HPLC-DAD	MWCNTs: o.d.: 30–60 nm	100	84–111	5.9–11 ng/L	1250 (sample volume: 500 mL; reconstitution volume: 0.4 mL)	Before use, MWCNTs were dried at 80 °C for 2 h	[83]
Thiamethoxam, imidacloprid and acetamiprid	Tap, ground and reservoir water	HPLC-UV	MWCNTs: o.d.: 30–60 nm	100	88–110	5.4–6.7 ng/L	125 (sample volume: 500 mL; elution volume: 4 mL)	Before use, MWCNTs were dried at 80 °C for 2 h	[84]
DDT ^a , DDD ^b and DDE ^c	Underground, tap and reservoir water	HPLC-UV	MWCNTs: o.d.: 30–60 nm	100	90–116	4.0–13 ng/L	500 (sample volume: 500 mL; reconstitution volume: 1 mL)	Before use, MWCNTs were dried at 80 °C for 2 h	[85]

Table 1 (Continued)

Analyte	Matrix	Method	CNTs characteristics	CNTs amount (mg)	Recovery (%)	LOD	Enrichment factor	Remarks	Reference
Dicamba	River water	HPLC-DAD	MWCNTs: o.d.: 5–10 nm	200	73	2.0 µg/L	33 (sample volume: 100 mL; elution volume: 3 mL)	Comparison between MWCNTs and C ₁₈ (MWCNTs were more effective)	[86]
Atrazine, propoxur and methidathion	Tap, reservoir and stream water	HPLC-DAD	MWCNTs: o.d.: 10–20 nm, 10–30 nm, 20–40 nm, 40–60 nm, 60–100 nm, length: 1–2 µm, 5–15 µm	200	81–108	37.5–220 ng/L	40 (sample volume: 400 mL; elution volume: 10 mL)	Effect of oxidation of MWCNTs with various oxidizing agents and effect of length and o.d. of MWCNTs were investigated	[87]
Carbofuran, iprobenfos, parathion-methyl, prometryn, fenitrothion, parathionethyl, isocarbofos, phenthoate, methidathion, endrin, ethion and methoxychlor	Milli-Q, tap and river water	GC-MS	MWCNTs: o.d.: 40–60 nm	100	82–104	10–30 ng/L	500 (sample volume: 500 mL; reconstitution volume: 1 mL)	Before use, MWCNTs were dried at 130 °C for 3 h	[88]
Metalaxyl, diethofencarb, myclobutanil, prometryn and tebuconazole	Tap, ground, rain and reservoir water	HPLC-UV	MWCNTs: o.d.: 30–60 nm	100	79–109	2.99–6.04 ng/L	1000 (sample volume: 500 mL; reconstitution volume: 0.5 mL)	Before use, MWCNTs were dried at 80 °C for 2 h	[89]
Triasulfuron and bensulfuron-methyl	Well, tap, sea and reservoir water	HPLC-DAD	MWCNTs: o.d.: 30–60 nm; specific surface area: 131.74 m ² /g	200	44–114	22.4 y 2.90 ng/L	1250 (sample volume: 500 mL; reconstitution volume: 0.4 mL)	Before use, MWCNTs were dried at 80 °C for 2 h	[90]
Nicosulfuron, triasulfuron, metsulfuron-methyl, thifensulfuron-methyl and bensulfuron-methyl	Tap, reservoir and well water, and seawater	HPLC-DAD	MWCNTs: o.d.: 30–60 nm	100	40–115	2.9–22.4 ng/L	1250 (sample amount: 500; reconstitution volume: 0.4 mL)	Before use, MWCNTs were dried at 80 °C for 2 h. Comparison with C ₁₈ (MWCNTs yielded higher recoveries)	[91]
α-HCH ^e , β-HCH ^e , γ-HCH ^e , δ-HCH ^e , DDE ^c , DDD ^b , DDT ^a , p,p'-DDT ^a	Lake and waste water	GC-ECD	SWCNTs: diameter <1–2 nm, length: 50 µm	2000	45–116	0.19–3.77 ng/L	– (sample volume: 10 mL)	SWCNTs as stationary phases of SPME fibers. Comparison with PDMS fiber (SWCNTs fiber exhibited higher sensitivity, longer life span, good precision and high thermal stability)	[92]
Diazinon	Tap water	HPLC-UV	MWCNTs: o.d.: 3–10 nm	50	94–97	60 ng/L	200 (sample volume: 1000 mL; elution volume: 5 mL)	Before use, MWCNTs were dried at 80 °C for 2 h	[93]
Parathion-methyl, paraoxon and fenitrothion	Garlic	SWV ^d	MWCNTs: –	–	97–104	5.0 µg/L	–	It is possible to control sorption and desorption at MWCNTs by electrochemical methods	[94]

Propoxur, atrazine and methidathion	Tap, reservoir and stream water	HPLC-DAD	MWCNTs: o.d.: 40–60 nm, length: 1–5 μm	200	81–108	36.0–220 ng/L	40 (sample volume: 400 mL; elution volume: 10 mL)	Comparison between MWCNTs, C_{18} silica and activated carbon (MWCNTs had more adsorption capacity)	[95]
Atrazine, deisopropyl-atrazine and deethyl-atrazine	Surface and underground water and agricultural soils	GC-MS	MWCNTs: i.d.: 40–60 nm, specific surface area: 40–300 m^2/g	100	72–110	Waters: 0.02–0.05 $\mu\text{g}/\text{L}$; soils: 0.3–1 $\mu\text{g}/\text{kg}$	Waters: 100 (sample volume: 100 mL; reconstitution volume: 1 mL); soils: (sample amount: 10 g; reconstitution volume: 1 mL)	–	[96]
Atrazine, dicloran, metazachlor and simazine	Tap and well water	HPLC-UV	MWCNTs: o.d.: 40–60 nm, length: 1–5 μm	300	85–95	5.0–15 ng/L	150 (sample volume: 600 mL; reconstitution volume: 4 mL)	MWCNTs adsorbent outperformed C_{18} bonded silica and graphitized carbon black	[97]
Ethoprofos, diazinon, chlorpyrifos-methyl, fenitrothion, malathion, chlorpyrifos, fenamiphos, and buprofezin	Apple, grape, orange and pineapple juices	GC-NPD	MWCNTs: o.d.: 10–15 nm, i.d.: 2–6 nm, length: 0.1–10 μm	40	73–103	1.91–7.32 $\mu\text{g}/\text{L}$	10 (sample volume: 10 mL; reconstitution volume: 1 mL)	Before use, MWCNTs were dried at 120 °C for 2 h	[98]
Fenpropathrin, cyhalothrin and deltamethrin	Tap, river, reservoir and well water	HPLC-UV	MWCNTs: o.d.: 30–60 nm	100	92–118	1.3–4.3 ng/L	500 (sample volume: 500 mL; reconstitution volume: 1 mL)	Before use, MWCNTs were dried at 80 °C for 2 h	[99]
Pirimicarb, pyrifenoxy, penconazol, carbendazim, cyromazine, pyrimethanil and cyprodinil	Milli-Q and mineral water	NACE-UV	MWCNTs: o.d.: 10–15 nm; i.d.: 2–6 nm, length: 0.1–10 μm	40	47–94	27–58 ng/L	750 (sample volume: 750 mL; reconstitution volume: 1 mL)	Before use, MWCNTs were dried at 120 °C for 2 h	[100]
Dichlorvos, methamidophos, acephate, omethoate, monocrotophos and dimethoate	Sea, reservoir and Milli-Q water	GC-FPD	Oxidized MWCNTs: (specific surface area: 200 m^2/g) and oxidized SWCNTs (o.d.: 0.8–1.6 nm, length: 5–30 μm , specific surface area: 380 m^2/g)	200	79–102	70–120 ng/L	100 (sample volume: 100 mL; elution volume: 1 mL)	Comparison between oxidized SWCNTs and Oasis HLB (oxidized SWCNTs could supplement Oasis HLB)	[101]
Carfentrazone-ethyl	Tap and river water	GC-ECD	MWCNTs: o.d.: 8.6 nm, i.d.: 3.5 nm, length: 0.5–1 μm	100	74–80	10 ng/L	500 (sample volume: 500 mL; reconstitution volume: 1 mL)	–	[102]
Atrazine, methidathion, and propoxur	Tap and reservoir water	UV-spectrophotometry	MWCNTs: o.d.: 40–60 nm, length: 1–5 μm	300	84–104	2–3 $\mu\text{g}/\text{L}$	150 (sample volume: 600 mL; reconstitution volume: 4 mL)	Use of multivariate calibration (partial least squares)	[103]
Fenpropathrin, cyhalothrin, deltamethrin, fenvalerate, tau-fluvalinate and biphenthrin	Tap, well, river and reservoir water	HPLC-UV	MWCNTs: o.d.: 30–60 nm, length: 5–30 μm , specific surface area: 131.74 m^2/g	100	71–118	0.7–4.3 ng/L	500 (sample volume: 500 mL; reconstitution volume: 1 mL)	Before use, MWCNTs were dried at 80 °C for 2 h	[104]

Table 1 (Continued)

Analyte	Matrix	Method	CNTs characteristics	CNTs amount (mg)	Recovery (%)	LOD	Enrichment factor	Remarks	Reference
Metsulfuron-methyl, chlorsulfuron, bensulfuron-methyl, pyrazosulfuron-ethyl, and chlorimuron-ethyl	Tap, well, river and canal water	HPLC-DAD	SWCNTs: o.d.: 1.5–2.5 nm, i.d.: 1.0–2.0 nm, specific surface area: 297.72 m ² /g	30	79–102	1.1–7.2 ng/L	3000 (sample volume: 3 L; reconstitution volume: 1 mL)	Use of SWCNTs disks and comparison with activated carbon disks and C ₁₈ disks (SWCNTs disks exhibited similar extraction ability)	[105]
Acetochlor, metolachlor and butachlor	Tap and reservoir water	GC-MS	MWCNTs: o.d.: 40–60 nm	100	89–116	2–6 ng/L	100,00 (sample volume: 100 mL; final volume: 10 µL)	Combination of SPE and DLLME	[106]
Ethoprophos, diazinon, chlorpyrifos-methyl, fenitrothion, malathion, chlorpyrifos, phosmet and buprofezin	Forestal, ornamental and agricultural soils	GC-NPD	MWCNTs: o.d.: 10–15 nm, i.d.: 2–6 nm, length: 0.1–10 µm	100	54–91	2.97–31.6 ng/g	– (sample amount: 1.5 g; reconstitution volume: 1 mL)	Before use, MWCNTs were dried at 120 °C for 2 h	[107]
Alachlor, acetochlor, metolachlor and butachlor	Tap and river water	GC-ECD	MWCNTs: o.d.: 8.6 nm, i.d.: 3.5 nm, length: 0.5–1000 µm	100	77–104	0.01–0.03 µg/L	500 (sample volume: 500 mL; reconstitution volume: 1 mL)	–	[108]
Carbendazim, thiabendazole, and thiophanate-methyl	River and untreated water	HPLC-UV	Oxidized MWCNTs: o.d.: 10–20 nm, length: 5–15 µm, specific surface area: 40–300 m ² /g	2.0	76–105	0.3–1.5 µg/L	57 (sample volume: 4 mL; eluent volume: 70 µL)	MWCNTs-COOH as an SPME fiber coating. Comparison between purified MWCNTs, MWCNTs-COOH, active carbon and carbograph (MWCNTs-COOH was superior to the rest of adsorbents)	[109]
Metsulfuron-methyl, chlorsulfuron, bensulfuron-methyl and chlorimuron-ethyl	Soil	HPLC-DAD	MWCNTs: o.d.: 40–60 nm	150	–	–	– (sample amount: 10 g; reconstitution volume: 15 µL)	Combination of dispersive solid-phase extraction and dispersive liquid–liquid microextraction. MWCNTs and C ₁₈ were used for the clean-up step. C ₁₈ provided the best results	[110]

–: Not indicated.

^a Dichlorodiphenyltrichloroethane.^b 1,1-Dichloro-2,2-bis-(4'-chlorophenyl)ethane.^c 1,1-Dichloro-2,2-bis-(4'-chlorophenyl)ethane.^d Square-wave voltammetry.^e Hexachlorocyclohexane.

Table 2
Applications of CNTs as SPE sorbents for the extraction of drugs from different samples.

Analyte	Matrix	Method	CNTs characteristics	CNTs amount (mg)	Recovery (%)	LOD	Enrichment factor	Remarks	Reference
Benzodiazepine residues: diazepam, estazolam, alprazolam and triazolam	Pork	GC-MS	MWCNTs: o.d.: 3–25 nm, length: 0.5–1000 μm	200	75–104	2–5 $\mu\text{g}/\text{kg}$	7.5 (sample volume: 7.5 mL; reconstitution volume: 1 mL)	Analytes were extracted by ultrasonic-assisted extraction	[111]
Sulfonamides: sulfadiazin, sulfamerazine, sulfadimidine, sulfathiazole, sulfamoxol, sulfamethizole, sulfamethoxy pyridazine, sulfachlorpyridazine, sulfadoxin and sulfisoxazole	Eggs and pork	HPLC-UV	MWCNTs: o.d.: 60–100 nm, length: 5–15 μm	80	66–86	4.1–10.0 ng/L	In the range between 37.7 and 160.9 (–)	Ultrasonic-assisted extraction and on-line SPE	[112]
Non-steroidal anti-inflammatory drugs: tolmetin, ketoprofen and indomethacine	Urine	CE-MS	Carboxylated SWCNTs immobilized on inert porous glass: i.d.: 0.7–1.2 nm, length: 2–20 μm	15 mg of the controlled pore glass containing SWCNT immobilized on its surface	99–102	1.6–2.6 $\mu\text{g}/\text{L}$	25 (sample volume: 5 mL; reconstitution volume: 200 μL)	–	[113]
Barbiturates: barbital, amobarbital and phenobarbital	Pork	GC-MS/MS	MWCNTs: o.d.: 20–40 nm, 40–60 nm, 60–100 nm	250	76–96	0.2–0.1 $\mu\text{g}/\text{kg}$	1.5 (sample volume: 7.5 mL; reconstitution volume: 5 mL)	Barbiturates were extracted by ultrasonic-assisted extraction and derivatized after SPE procedure	[114]
Tetracyclines: tetracycline, oxytetracycline and doxycycline	Surface water	CE-MS	SWCNTs: o.d.: 1.2–1.5 nm, 0.7–1.2 nm, length: 2–5 μm , 2–20 μm ; MWCNTs: o.d.: 20–50 nm Length: 5–20 μm	6	99–103	0.30–0.69 $\mu\text{g}/\text{L}$	50 (sample volume: 10 mL; reconstitution volume: 200 μL)	Only MWCNTs provided adequate results	[115]
Cephalotin, cephalexin, cephradine, cephaclor, sulfathiazole, sulfadiazine, sulfapyridine, sulmethazine, phenol, benzoic acid, hydroxyquinone, guaiacol, 1,3,5-trihydroxybenzene and 3,5-dihydroxybenzoic acid	Tap and well water	HPLC-UV	MWCNTs: o.d.: 30–60 nm; SWCNTs: o.d.: 0.5–1.6 nm	100	55–102	27–38 ng/L	50 (sample volume: 500 mL; elution volume: 10 mL)	Retention abilities of C_{18} and graphitized carbon black were also investigated	[116]
Antidepressants: imipramine, desipramine, amitryptiline, nortryptiline, clomipramine, trimipramine, trazodone, fluoxetine and mianserine	Urine	HPLC-UV	MWCNTs: o.d.: 20–50 nm, length: 5–20 μm	30	72–97	12.3–50.0 $\mu\text{g}/\text{L}$	40 (sample volume: 20 mL; reconstitution volume: 500 μL)	Use of ionic liquids to improve the HPLC chromatographic behavior of the analytes	[117]

–: Not indicated.

Table 3
Applications of CNTs as SPE sorbents for the extraction of different compounds (including phthalate esters and phenolic compounds) from different samples.

Analyte	Matrix	Method	CNTs characteristics	CNTs amount (mg)	Recovery (%)	LOD	Enrichment factor	Remarks	Reference
Bisphenol A, 4- <i>n</i> -nonylphenol and 4- <i>tert</i> -octylphenol	Tap, river, sea and waste water	HPLC-FLD	MWCNTs o.d.: 30–60 nm	500	90–104	18–83 ng/L	200 (sample volume: 500 mL; elution volume: 2.5 mL)	Comparison between MWCNTs, C ₁₈ and XAD-2 copolymer (MWCNTs exhibited a better property for the extraction of all analytes)	[118]
Di-ethyl-phthalate, di- <i>n</i> -propyl-phthalate, di- <i>iso</i> -butyl-phthalate and di-cyclohexyl-phthalate	Tap, river and sea water	HPLC-DAD	MWCNTs o.d.: 30–60 nm	500	68–105	180–860 ng/L	200 (sample volume: 1 L; elution volume: 5 mL)	Comparison between MWCNTs, C ₁₈ , C ₈ , and PS-DVB (were more effective than or as effective as these adsorbents for the SPE extraction of the analytes)	[119]
4- <i>n</i> -Nonylphenol, 4- <i>tert</i> octylphenol, bisphenol A; di- <i>n</i> -propyl-phthalate, di- <i>n</i> -butyl-phthalate, di-cyclohexyl-phthalate and di- <i>n</i> -octyl-phthalate, 3-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol	Tap, river and waste water	HPLC-FLD	SWCNTs: o.d.: 1.5–2.5 nm, i.d.: 1.0–2.0 nm, Specific surface area: 297.72 m ² /g	30	59–100	7.0–38 ng/L	1000 (sample volume: 1 L; reconstitution volume: 1 mL)	Use of SWCNTs disks and comparison with activated carbon disks and C ₁₈ disks (SWCNTs disks can extract polar chlorophenols more efficiently than the other disks)	[120]
4-Chlorophenol, 3-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol	Tap and river water	HPLC-UV	MWCNTs: o.d.: 30–60 nm, specific surface area: 131.74 m ² /g	300	88–109	80–800 ng/L	200 (sample volume: 200 mL; reconstitution volume: 1 mL)	–	[121]
2-Nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, 2,4-dichlorophenol and 2,4-dimethylphenol	River and waste water	HPLC-UV	Oxidized MWCNTs: o.d.: 10–20 nm, length: 5–15 μm	2	24–119	0.25–3.67 μg/L	57 (sample volume: 4 mL; desorption volume: 70 μL)	Oxidized MWCNTs as stationary phases of SPME fibers	[122]
Pentachlorophenol, 2,4,5-trichlorophenol, 3,3',4,4'-tetrachlorobiphenyl and 2,2',5,5'-tetrabromobiphenyl	River water	GC-ECD	Pristine MWCNTs, oxidized MWCNTs, and MWCNTs functionalized with polyethylene glycol (MWCNTs-PEG) and octadecylamine (MWCNTs-ODA)	20	55–100	1.0–6.0 μg/L	10 (sample volume: 100 mL; reconstitution volume: 10 mL)	Good recoveries, especially when MWCNTs-ODA were used as adsorbents	[123]
2-Chlorophenol, 2,3-dichlorophenol, 2,4-dichlorophenol, 2,3,5-trichlorophenol, 2,4,5-trichlorophenol and pentachlorophenol	Drinking, swimming pool, water-tank and well water	GC-MS	Carbon nanocones/disks nanocones: 300–800 nm length, 1–2 μm diameter, 20–50 nm thickness. Disks: 0.8–3 μm diameter, 20–50 nm thickness	20	99–101	0.3–8 μg/L	160–320 (sample volume: 8 mL; reconstitution volume: 25–50 μL)	Comparison between carbon nanocones/disks and MWCNTs (it was necessary the use of high elution volume to achieve the quantitative elution of the target pollutants from MWCNTs)	[124]

4-Nitrophenol	Lake water	Linear sweep voltammetry	Single-walled carbon nanohorn (SWCNH)	2.5	92–106	1.1×10^{-8} M	–	Comparison with bare glassy carbon electrode (GCE) and MWCNT-modified GCE (the sensitivity at SWCNH-modified GCE increases by 51.6 times and 5.55 times, respectively)	[125]
Phenol, <i>p</i> -nitrophenol, <i>m</i> -methylphenol, bisphenol A, 2-chlorophenol and 2,4-dichlorophenol	Sea and tap water	HPLC-UV	SWCNTs: specific surface area: 380 m ² /g	0.4–0.9	88–102	0.9–3.8 μg/L	100 (sample volume: 10 mL; desorption volume: 0.1 mL)	Electrophoretic deposition was used to prepare SPME fiber coated with SWCNTs	[126]
2-Chlorophenol, 2,4-dichlorophenol, 2-methylphenol, 3-methylphenol, 2,6-dimethylphenol and 2-nitrophenol	Lake water	GC-FID	MWCNTs: –	100	88–116	1.05–65.9 ng/L	– (sample volume: 10 mL)	MWCNTs-polyaniline composite film as stationary phases of SPME fibers, which was fabricated by electrochemical polymerization	[127]
2-Nitrophenol, 2,6-dichloroaniline and naphthalene	Distilled water	HPLC-UV	SWCNTs and MWCNTs: –	0.3	–	0.1–3 μg/L	25–60 (sample volume: 3–5 mL; eluent volume: 50–200 μL)	μ-SPE. Comparison was made with C ₁₈ , self-assembled, SWCNTs and MWCNTs	[128]
<i>p</i> -Nitroaniline, <i>m</i> -cresol, aniline, phenol and <i>o</i> -dinitrobenzene	Pond water	GC-FID	MWCNTs/Nafion: diameter: <5 nm, length: 5–15 μm, specific surface area: 400 m ² /g	–	83–106	0.03–0.57 μg/L	– (sample volume: 5 mL)	Comparison with PA fiber (extraction results using the MWCNTs/Nafion coated fiber were better than those obtained by PA fiber)	[129]
16 volatile organic compounds	Air and water	GC-FID	Purified MWCNTs: o.d.: 15–30 nm, i.d.: 3 nm, specific surface area: 98 m ² /g	650	82–111	–	–	Use of a purge-and-trap system to preconcentrate analytes from samples. The adsorption property of purified MWCNTs was studied and compared with those of Carboxen 100 and VOCARB 3000	[130]
1,2-Dichlorobenzene, 1,2,4-trichlorobenzene, 1,2,4,5-tetrachlorobenzene and hexachlorobenzene	River water	GC-MS	MWCNTs: o.d.: 30–60 nm, i.d.: 5–30 nm, specific surface area: 132 m ² /g	15	80–103	80–600 ng/L	50 (sample volume: 100 mL; reconstitution volume: 2 mL)	Comparison between MWCNTs, C ₁₈ silica and activated carbon (MWCNTs had the highest adsorption capacity)	[131]
N _α -Benzoyl-L-Arginine, N _α -Z-L-Arginine, N _α -Benzoyl-L-arginine ethyl ester hydrochloride, N _α -benzoyl-DL-arginine-4-nitroanilide, peptides of Leu-Tyr and Leu-Met, propranolol, cinchonine and quinine	Urine	MALDI-TOF-MS	MWCNTs: –	10	–	–	9 (sample volume: 9 μL; final volume: 1 μL)	With the addition of glycerol and sucrose into the dispersant, the intensity, S/N, and resolution of peaks for analytes by MS increased significantly	[132]

Table 3 (Continued)

Analyte	Matrix	Method	CNTs characteristics	CNTs amount (mg)	Recovery (%)	LOD	Enrichment factor	Remarks	Reference
2,2',4,4'-TetraBDE, 2,2',4,4',5-pentaBDE, 2,2',4,4',6-pentaBDE, 2,2',4,4',5,5'-hexaBDE and 2,2',4,4',5,6'-hexaBDE	River water, waste water and milk	GC-ECD	MWCNTs: diameter: 20–40 nm, length: 5–15 μ m, specific surface area: 40–300 m ² /g	–	90–119	3.6–8.6 ng/L	– (sample volume: 10 mL)	MWCNTs as stationary phases of SPME fibers. Comparison with activated carbon and PDMS-DVB (the use of MWCNTs provided higher enhancement factors)	[133]
Basic proteins (hemoglobin and cytochrome c)	Human blood	UV-vis spectrophotometry	MWCNTs: o.d.: 60–100 nm, length: 5–15 μ m, specific surface area: 40–300 m ² /g	8–10	90–98	60–120 μ g/L	10 (sample volume: 2 mL; eluent volume: 200 μ L)	On-line SPE. Use of MWCNT-packed microcolumn (μ -SPE). MWCNTs were oxidized with nitric acid to create a negatively charged MWCNT surface	[134]
Naphthalene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, ben[a]anthracene, benzo[b]fluoranthene and benzo[k]fluoranthene	Tap and river water	HPLC-UV	o.d.: 30–50 nm	500	79–117	5–58 ng/L	125 (sample volume: 500 mL; elution volume: 4 mL)	Comparison with C ₁₈ (the MWCNTs packed cartridge gave more efficient extraction performance for PAHs from aqueous solution)	[135]
C ₁₀ , C ₁₁ , C ₁₂ and C ₁₃ linear alkylbenzene sulfonates	River water	HPLC-UV	Carboxyl modified multi-walled carbon nanotubes (CMMWCNTs): o.d.: 30–60 nm, length: 30 μ m, specific surface area: 110 m ² /g; MWCNTs: o.d.: 30–50 nm	200	85–106	20–30 ng/L	1000 (sample volume: 500 mL; reconstitution volume: 0.5 mL)	Comparison between CMMWCNTs, C ₈ and C ₁₈ (CMMWCNTs cartridge showed stronger retention ability than C ₈ or C ₁₈ cartridges for target compounds)	[137]
CS ⁺ : dodecylethyl dimethyl ammonium bromide, methyltrioctyl ammonium chloride, cetyltrimethylammoniumbromide and cetylpyridinium chloride	River and waste water	AP-MALDI-MS	Oxidized MWCNTs: diameter: 10–20 nm, length: 5–15 μ m, specific surface area: 40–300 m ² /g	100	91–98	10–15 ng/L	25–35 (–)	Oxidized MWCNTs as sorbents for MSPD	[138]
4-Nitroaniline, 2-nitroaniline, 2-chloroaniline and 2,4-dichloroaniline	River and waste water	HPLC-UV	Oxidized MWCNTs: o.d.: 20–40 nm, length: 5–15 μ m	–	56–110	40–130 ng/L	– (sample volume: 40 mL)	Oxidized MWCNTs as an in-tube SPME medium	[139]
3,3',4-Tribromodiphenylether, 2,2',4,4'-tetrabromodiphenylether, 3,3',4,4'-tetrabromodiphenylether, 2,2',4,4',5-pentabromodiphenylether, 2,2',4,4',6-pentabromodiphenylether, 2,2',4,4',5,5'-hexabromodiphenylether and 2,2',4,4',5,6'-hexabromodiphenylether	Reservoir and waste water	GC-ECD	SWCNTs: diameter <2 nm, length: 5–15 μ m, specific surface area: 400 m ² /g	90	74–109	0.08–0.8 ng/L	– (sample volume: 10 mL)	SWCNTs were functionalized with an hydroxyl-terminated silicone oil. This product was used as precursor and selective stationary phase to prepare the sol-gel derived poly (SWCNTs-TSO-OH) SPME fiber. HS-SPME. Comparison with commercial SPME fibers	[140]

27 amines; anilines, chloroanilines, N-nitrosamines and aliphatic amines	River, pond, tap, well, drinking, swimming pool and waste water	GC-MS	MWCNTs: i.d.: 2–15 nm, length: 1–10 μm , 5–20 graphitic layers	80	-	-	-(sample volume: 300 mL)	On-line SPE. Comparison of several SPE sorbents: LiChrolut EN, Oasis HLB, RP-C ₁₈ , graphitized carbon black, fullerenes and MWCNTs (LiChrolut EN and Oasis HLB were the only materials in which all the amines assayed were quantitatively retained)	[141]
Bovine hemoglobin and serum albumin	Human blood	UV-vis spectrophotometry	MWCNTs: -	15	90	1.0 mg/L	10 (sample volume: 2 mL; eluent volume: 200 μL)	MWCNTs functionalized with poly(diallyldimethylammonium chloride).	[142]
Benzene, 1-butanol, pyridine, 2-pentanone, nitropropane	Distilled water	GC-MS	Hydroxylated MWCNTs	2	-	-	-	On-line SPE Hydroxylated MWCNTs-coated SPME metal fiber based on sol-gel technique. Comparison with PDMS fiber	[143]

-: Not indicated.

protocol with Milli-Q water and adjust the pH at 6.0 of 10 mL of juice prior to the MWCNTs-SPE procedure. Mean recovery values in this case were above 73% for all pesticides and fruit juices (between 77 and 101% for apple juice, 75 and 103% for grape juice, 73 and 103% for orange juice and 73 and 93% for pineapple juice) and LODs were also well below the EU MRLs established for these compounds in raw fruits. Matrix-matched calibration was found necessary to correctly quantify the selected pesticides in the mentioned fruit juices. The obtained results showed that this method was quick, cheap, accurate and highly selective. In addition, in both works [72,98] small amounts of inexpensive MWCNTs (40 mg) of low o.d. were employed. In fact, this research group developed an economic study with the CNTs used [100] and it was found that in Spain, 5 g of the selected MWCNTs cost approximately 56.80 € in 2008. In these specific applications [72,98] as well as in another work of the same group [100], with 5 g of CNTs, up to 125 extractions can be developed, which represents a cost of approximately 0.45 € per extraction. This cost is much lower than that of conventional SPE cartridges, which is clearly an important advantage of the use of these extraction materials.

As it can be seen in Table 1, the use of such low quantities of CNTs as stationary phases is not very common [46,72,74,93,98,100,105,109]. Another example is the work developed by López-Feria et al. [74] who reported a rapid one-step methodology for the quantitative extraction of chlortalone, diuron, atrazine, simazine, terbuthylazin-desethyl, dimethoate, malathion and parathion from virgin olive oil prior to their analysis by GC-MS. For this purpose, MWCNTs and carboxylated SWCNTs (c-SWCNTs) were evaluated, the later being the most appropriate in terms of sorption capability. After evaluating the influence of the sorbent amount (between 10 and 50 mg) authors observed that peak analyte area increased for all pesticides when increasing the amount of sorbent up to 30 mg. Apart from the kind and amount of stationary phase, other parameters such as sample volume and dilution, and type and volume of eluent were evaluated, finding that the best conditions were 3 mL of virgin olive oil:hexane sample solution (20:80 v/v) and 0.5 mL of ethyl acetate as eluent. Under all these conditions, good linearity, reproducibility and low LODs (1.5–3.0 $\mu\text{g/L}$) were achieved. Moreover, the 30 mg packed cartridge could be reused for at least 100 samples without losing retention capacity.

Concerning the studied samples, only in seven cases non-aqueous samples have been analyzed. This is the case of the analysis of pesticides in garlic extracts [94], soils [96,107,110], fruit juices [98], virgin olive oil [74] and sewage sludge [46]. Apart from the previously mentioned works of López-Feria et al. [74] and Ravelo-Pérez et al. [98] in which olive oil and fruit juices were analyzed, respectively, it is also worth mentioning the work of Asensio-Ramos et al. [107] who developed a simple and cost-effective MWCNTs-SPE method with the aim of determining seven organophosphorus pesticides (*i.e.*, ethoprophos, diazinon, chlorpyrifos-methyl, fenitrothion, malathion, chlorpyrifos and phosmet) and one thiazidine (buprofezin) in forestal, ornamental and agricultural soils using GC-NPD. This method involved an ultrasound-assisted extraction of the soils followed by a MWCNTs-SPE procedure as clean-up step using also low cost CNTs (10–15 nm o.d., 2–6 nm i.d. and 0.1–10 μm length). Good linearity, precision, recovery, accuracy and selectivity parameters were assayed, and matrix effects were also studied, which revealed that suitable matrix-matched calibration should be developed. LODs were in the range of 2.97–31.6 ng/g.

Some of the works shown in Table 1 have focused on the comparison of the extraction efficiency between CNTs [74,87] and other stationary phases such as C₁₈ [75,82,86,91,95,97,105], activated carbon [82,95,97,105,109], Oasis HLB [101] and PDMS [92]. In most cases, CNTs generally exhibited higher sorption capability than the other sorbents mentioned or at least as effective. One of

these works was developed by Zhou et al. [75] who compared the enrichment performance of C_{18} and MWCNTs for the extraction of cyanazine, clorotoluron and chlorbenzuron from environmental water samples (*i.e.*, tap, ground, snow and sewage water) and later analysis by HPLC–UV. The developed method, which involved the use of 100 mg of MWCNTs, 250 mL of sample at pH 7 and 5 mL of dichloromethane as eluent, showed a higher stability and larger potential to be widely used for the analysis of these analytes at trace levels in the mentioned samples. Though MWCNTs were reused more than 200 times, excellent spiked recoveries in the range of 88–110% were achieved from all the water samples for the three pesticides. Moreover, the comparison between MWCNTs and C_{18} showed that MWCNTs were at least as effective as C_{18} for cymazine and chlorotoluron but they were more effective for chlorbenzuron.

Pesticide determination after CNTs–SPE procedure has been mainly carried out by HPLC [71,75,82–87,89–91,93,95,97,99,104,105,109,110] and GC [46,72,74,88,92,96,98,101,102,106,107,108] in combination with UV, DAD or MS, see Table 1. Moreover, up to now, there only exists one work in the literature concerning the use of CE after the extraction of pesticides by CNTs as stationary phases [100]. In this work, Asensio-Ramos et al. determined a group of seven pesticides (*i.e.*, pirimicarb, pyrifenox, penconazol, carbendazim, cyromazine, pyrimethanil and cyprodinil) in Milli-Q and mineral water samples using NACE with UV detection after their extraction by SPE with MWCNTs of low o.d. as stationary phase (10–15 nm o.d., 2–6 nm i.d. and 0.1–10 μ m). Ametryn was used as internal standard. Optimum BGE, consisting of a mixture of methanol and acetonitrile (1:2 v/v) with 90 mM sodium dodecyl sulfate (SDS) and 20.5 mM $HClO_4$, was satisfactory to get a good resolution of the seven compounds in less than 13 min. In order to increase the sensitivity and achieve low LODs, on-line preconcentration by electrokinetic injection of the sample dissolved in 78:22 v/v acetonitrile/methanol, 1.11 mM $HClO_4$, and off-line preconcentration by SPE with 40 mg of MWCNTs were carried out. Fig. 2 shows the SPE–NACE–UV electropherograms of a spiked and non-spiked mineral water sample using the BGE optimized at the beginning of the experiment (Fig. 2 a and b) and a slightly modified BGE (Fig. 2c) due to the presence of some interferences of the sample matrix. Results showed that increasing SDS concentration allowed obtaining complete resolution of the pesticides and interferences. Under these conditions, mean recovery values ranged between 47 and 94% for all pesticides in all samples and LODs were in the range 27–58 ng/L, well below EU MRLs.

2.1.2. Pharmaceuticals

Drugs such as antibiotics, anxiolytics, anti-inflammatories or antidepressants have also been extracted using CNTs as SPE sorbents. These studies are summarized in Table 2. Concerning the extraction of antibiotics using CNTs–SPE, sulfonamides have been analyzed in eggs and pork [112], tap and well water [116], tetracyclines in surface water [115] and cephalosporins in tap and well water [116]. In all these works different SPE sorbents were compared. This is the case of the work of Fang et al. [112] in which MWCNTs and C_{18} were compared for the extraction of sulfonamides from eggs and pork, or the work of Niu et al. [116] that compared the use of MWCNTs, SWCNTs, C_{18} and graphitized carbon black for the extraction of sulfonamides from waters. Also Suárez et al. [115] made a comparison between MWCNTs and SWCNTs for the extraction of tetracyclines from surface waters, while Niu et al. [116] studied both MWCNTs and SWCNTs which were compared with C_{18} and graphitized carbon black for the extraction of cephalosporins from tap and well water. In all cases, sorption capabilities of MWCNTs were clearly higher than the capabilities of the other stationary phases. It is worth mentioning the work of Niu et al. [116], who investigated the applicability of the CNTs as packing SPE sorbents for the extraction of sulfonamides, cephalosporins

and phenolic compounds from tap and well water prior their HPLC–UV determination. Extraction capability of MWCNTs, SWCNTs, C_{18} and graphitized carbon black were compared. Since compounds with more than one amino group or hydroxyl group are more difficult to desorb using CNTs or graphitized carbon black, great efforts were made to optimize the desorption conditions. The best eluent was made of 30% (v/v) of 0.3 M ammonium acetate water solution and 70% (v/v) of methanol. Satisfactory recoveries of the analytes were obtained, which were in the range of 80–100%. Comparative studies with different SPE sorbents showed that, in general, antibiotics were more strongly retained on MWCNTs sorbents than on C_{18} or graphitized carbon black. Regarding the analytical methods employed for the analysis of antibiotics, HPLC has been used in most works although in one of them CE was preferred. In this study, developed by Suárez et al. [115], tetracycline residues (*i.e.*, tetracycline, oxytetracycline and doxycycline) were preconcentrated from environmental water samples at trace levels using MWCNTs (o.d. 20–50 nm). For this purpose, a flow system was coupled at-line to the CE–MS equipment which had an ESI interface. For the ESI, a sheath-liquid composed of 50:50 (v/v) methanol/water containing 0.5% (v/v) formic acid was used at 4 μ L/min flow rate. Optimum running buffer was 50 mM formic acid at pH 2.0. The use of low amounts of CNTs made the at-line coupling of the flow preconcentration unit to the CE–MS especially interesting allowing the simple elution of analytes in a low volume of eluent. Moreover, MWCNTs and two other SWCNTs were compared, showing that MWCNTs had higher sorption capabilities.

As it can also be seen in Table 2, anxiolytics like benzodiazepines [111] or barbiturates [114] have been extracted from pork tissues using MWCNTs after a previous ultrasound-assisted extraction procedure and then analyzed by GC–MS or GC–MS/MS. In both cases, SPE enrichment and clean-up required relatively high quantities of stationary phase (200 and 250 mg of MWCNTs for the extraction of benzodiazepines and barbiturates, respectively). Regarding the extraction of benzodiazepines, Wang et al. [111] developed a SPE–GC–MS method using MWCNTs of 3–25 nm o.d. for the determination of diazepam, estazolam, alprazolam and triazolam. Ultrasonic extraction conditions (*i.e.*, temperature, time, power and solvent volume) and SPE parameters (*i.e.*, sample amount, variety and volume of eluent) were optimized. Optimum conditions (*i.e.*, 10 min of ultrasound-assisted extraction of 5 g of sample at 30 °C and 60% power with 40 mL of acetonitrile and elution with 5 mL of hexane for SPE) allowed the achievement of recoveries between 75 and 104% with LODs in the range 2–5 μ g/kg. Authors also compared the absorption capability of MWCNTs with that of C_{18} in the static condition, selecting diazepam as target compound. The obtained results showed that static absorption capability of MWCNTs was higher than that of C_{18} under the same experimental conditions and thus a lower amount of sorbent was required for cartridges using MWCNTs. On the other hand, Zhao et al. [114] also compared the overall extraction efficiency of MWCNTs and C_{18} for the preconcentration of three barbiturates (*i.e.*, barbital, amobarbital and phenobarbital) in pork and subsequent analysis and confirmation was carried out by GC–MS/MS. Results indicated that MWCNTs packed cartridges and C_{18} SPE cartridges had similar enrichment abilities for barbital and amobarbital, while the use of MWCNTs showed a stronger enrichment ability than that of C_{18} towards phenobarbital. Moreover, in this work a comparison between three different derivatization methods was made, including microwave assisted derivatization, ultrasound assisted derivatization and thermal incubation derivatization. The first of these procedures was found more effective and rapid (8 min) for methyl derivatization of the barbiturates.

Concerning anti-inflammatories, there is only one work in the literature regarding the extraction of this type of drugs using CNTs as SPE sorbents. In this study, Suárez et al. [113] demonstrated for

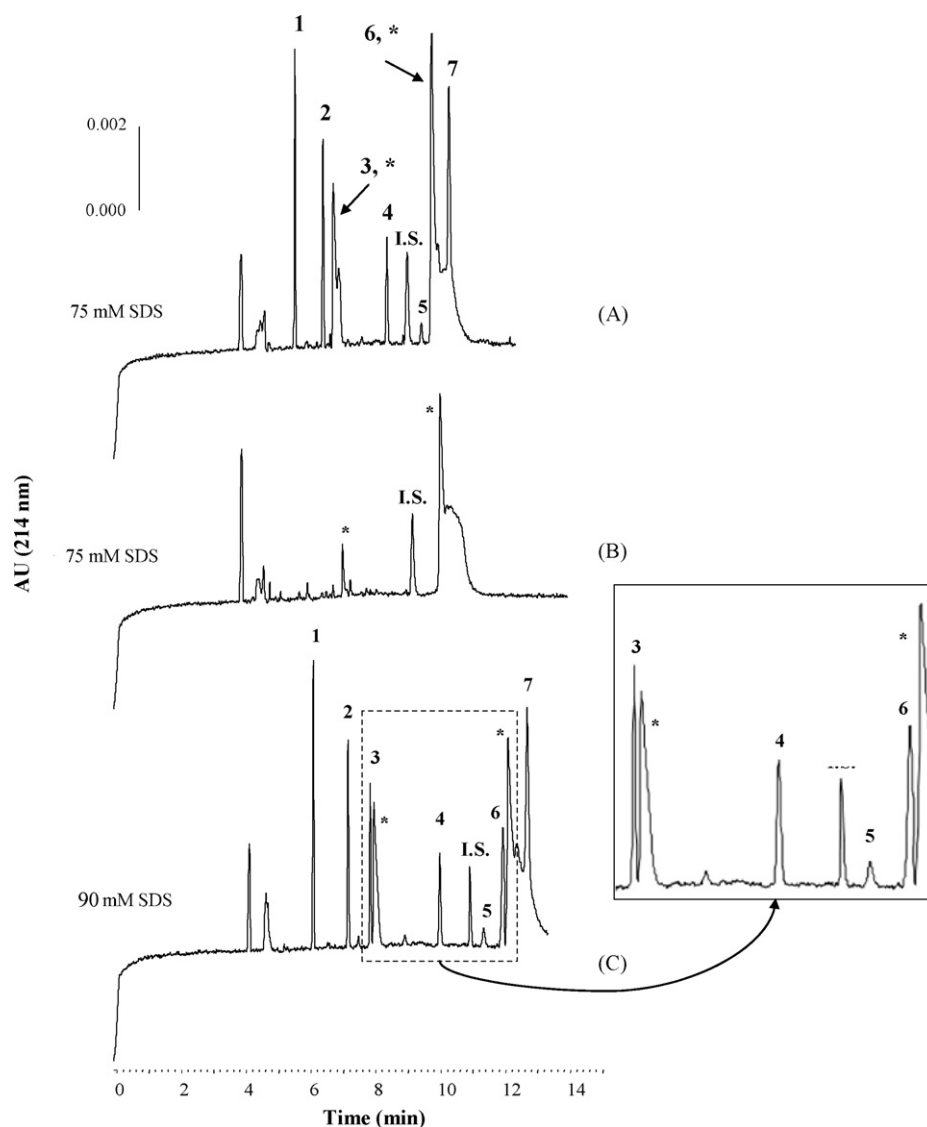


Fig. 2. SPE-NACE-UV electropherograms of a spiked and non-spiked mineral water sample containing approximately $0.7 \mu\text{g/L}$ of each pesticide at pH 8 using the BGE optimized at the beginning of the experiment: 70 mM SDS, 20.5 mM HClO_4 in 1:2 v/v MeOH/ACN (a and b) and a spiked mineral water sample containing the same concentration of each pesticide, but using a slightly modified BGE: 90 mM SDS, 20.5 mM HClO_4 in 1:2 v/v MeOH/ACN (c). Sample in 78:22 v/v ACN/MeOH, 1.11 mM HClO_4 . Total length of the capillary, 60.2 cm (50 cm effective length); voltage, 22 kV; UV detection at 214 nm; electrokinetic injection for 12 s at +10 kV. Reprinted from [100] with permission from Elsevier.

the first time that laboratory immobilized carboxylated SWCNTs (*c*-SWCNTs) on a controlled porous glass surface had a high sorption capacity to retain non-steroidal anti-inflammatories (*i.e.*, tolmetin, ketoprofen and indomethacin) due to the special orientation of the immobilized *c*-SWCNTs. In this specific case, a minicolumn was constructed by packing 15 mg of a controlled-pore glass containing *c*-SWCNTs immobilized on its surface. Coupling of CNTs with the previously activated glass (see the work for details) was carried out leaving the glass for 5 h in contact with the *c*-SWCNTs and dimethylformamide containing 1,3-dicyclohexylcarbodiimide. The developed method was applied to the analysis of urine samples using CE-MS, allowing the detection of concentrations of 1.6–2.6 $\mu\text{g/L}$ for all the analytes with only 5 mL of sample (recoveries ranged between 98.6 and 102.2%).

Antidepressants have also been studied only in one occasion. In this work, developed by Cruz-Vera et al. [117], nine antidepressants including tricyclic antidepressants and selective noradrenalin or serotonin reuptake inhibitors (*i.e.*, imipramine, desipramine, amitriptyline, nortriptyline, clomipramine, trimipramine, trazodone, fluoxetine and mianserine) were also determined in urine samples

using MWCNTs-SPE-HPLC-UV. Chromatographic separation was achieved in a reversed-phase C_8 column using the ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate as silanol activity suppressor, which enhances peak symmetry and chromatographic resolution. The method was validated for sensitivity and precision and LODs achieved were in the range 12.3–90.1 $\mu\text{g/L}$ (recoveries ranged between 72 and 97%).

2.1.3. Phthalate esters, phenolic compounds and others

Besides pesticides and drugs, CNTs have also been used for the extraction of other organic compounds, such as phthalate esters [118–120], phenolic compounds [121–129] and others [130–143]. Table 3 compiles all these applications. Regarding phthalate esters, several research studies have shown the suitability of CNTs for the adsorption of these compounds from water samples [118–120]. Moreover, in all these studies analytes were determined using HPLC with either FLD [118,120] or DAD [119]. One example is the work carried out by Cai et al. [118] in which a simple and rapid method was developed for the SPE of three endocrine disruptors (bisphenol A, 4-*n*-nonylphenol and 4-*tert*-octylphenol) from

tap, river, sea and waste water by using a MWCNTs packed cartridge (o.d. 30–60 nm). Analytes were quantitatively desorbed with suitable amounts of methanol and finally they were determined by HPLC-FLD. After evaluating the effects of different parameters affecting the SPE on the recoveries of the analytes, comparative studies were carried out with C₁₈ and XAD-2 PS-DVB copolymer following the same experimental procedure and conditions as with the MWCNTs packed cartridge. The obtained results showed that MWCNTs were at least as effective as C₁₈ for the SPE of 4-*n*-nonylphenol and 4-*tert*-octylphenol, but they were more effective than C₁₈ for the SPE of bisphenol A. Compared with XAD-2 PS-DVB copolymer, they exhibited better ability for the extraction of all the three analytes. This work was the first application of MWCNTs as packing materials for the SPE of organic pollutants from aqueous solutions before they were analyzed by chromatographic methods. These authors also studied in a second work [119] the extraction of another group of phthalate esters including di-ethyl-phthalate, di-*n*-propyl-phthalate, di-*iso*-butyl-phthalate and di-cyclohexyl-phthalate from tap, river and sea water using the same type and amount of MWCNTs. HPLC-DAD was also used. Under optimized extraction conditions (*i.e.*, 1000 mL of sample, flow rate of 8 mL/min and 5 mL of acetonitrile as elution solvent), LODs in the range 0.18–0.86 ng/mL and recoveries between 68 and 105% were achieved for the four phthalate esters. These recoveries were compared with the ones obtained using several commercial SPE adsorbents, including C₁₈, C₈ and PS-DVB, and the results showed that MWCNTs were more effective than or as effective as these adsorbents for all the analytes. With the optimized methods, several samples were analyzed. However, no phthalate esters were found in river and sea water samples. Concerning tap water, di-ethyl-phthalate, di-*n*-propyl-phthalate, and di-cyclohexyl-phthalate were not found, only 2.0 ng/mL of di-*iso*-butyl-phthalate were detected.

SWCNTs have also been employed with the aim of simultaneously extracting phthalate esters and chlorophenols. This is the case of the work of Niu et al. [120] who developed a new, easy-to-make and practical SPE disk based on a sheet of SWCNTs to preconcentrate 4-*n*-nonylphenol, 4-*tert*-octylphenol, bisphenol A; di-*n*-propyl-phthalate, di-*n*-butyl-phthalate, di-cyclohexyl-phthalate, di-*n*-octylphthalate, 3-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol prior to their determination by HPLC-FLD. The perfect mechanical properties and the larger specific area of the disk allowed the use of higher flow rates. Moreover, one liter of aqueous solution could be passed through the disk within 10–100 min while still allowing good recoveries (between 59 and 100%). The effect of the number of layers of stacked disks was also investigated, finding out that a double-disk system improved the extraction ability of the SWCNTs disks more efficiently than the single-disk or the triple-disk systems. A comparison study with SWCNTs disks, activated carbon disks and C₁₈ disks showed that SWCNTs disks could extract analytes more efficiently than the other disks.

As it can be seen in Table 3, the use of CNTs as sorbent materials for the extraction of phenolic compounds has only been investigated for water samples [121–129]. For these studies, different phenolic compounds were determined by using HPLC [121,122,126,128], GC [123,124,127,129] or even linear sweep voltammetry [125]. Moreover, different types of CNTs were used, including non-functionalized MWCNTs [121,123,127,128], functionalized MWCNTs [122,123], carbon nanocones/disks [124], single-walled carbon nanohorn (SWCNH) [125], non-functionalized SWCNTs [126,128] and MWCNTs/nafion [129], mainly in low quantities [122–126,128]. As an example, Salam and Burk [123] investigated the application of non-functionalized and chemically modified MWCNTs (*i.e.*, oxidized MWCNTs and MWCNTs functionalized with polyethylene glycol, MWCNTs-PEG,

or with octadecylamine, MWCNTs-ODA) as packing materials for the preconcentration and GC-ECD determination of various polyhalogenated organic pollutants, including pentachlorophenol, 2,4,5-trichlorophenol, 3,3',4,4'-tetrachlorobiphenyl and 2,2',5,5'-tetrabromobiphenyl from river water based on SPE. The obtained results showed that MWCNTs-ODA had the highest adsorption capacities for the four analytes under investigation, polar and non-polar, followed by the non-functionalized MWCNTs and then MWCNTs-PEG. The regeneration and reusability of the different MWCNTs-SPE cartridges were also studied and results showed that they could be used for three times with no loss of efficiency. LODs achieved were between 1.0 and 6.0 µg/L and recoveries ranged 55–100%. Jiménez-Soto et al. [124] evaluated the potential of carbon nanocones/disks as a new nanostructured carbon sorbent in SPE for the determination of chlorophenols (*i.e.*, 2-chlorophenol, 2,3-dichlorophenol, 2,4-dichlorophenol, 2,3,5-trichlorophenol, 2,4,5-trichlorophenol and pentachlorophenol) in drinking, swimming pool, water-tank and well water by using GC-MS. Carbon nanocones/disks consisted of 20% (w/w) carbon nanocones and 70% (w/w) carbon disks, being the rest amorphous carbon. The percentage of amorphous material had been reduced by thermal treatment of the commercial product by heating the raw material at 450 °C for 20 min, achieving a marked increase of the sorbent properties in terms of reversibility of the interaction analyte-sorbents. LODs of chlorophenols were in the range 0.3–8 µg/L and average recovery values were between 99 and 101% for all analytes in all samples. The performance of the carbon nanocones/disks as sorbent material was compared with that of MWCNTs, finding out that MWCNTs required the highest volume for the elution of the analytes from the cartridge which resulted in lower preconcentration factors and subsequent higher LODs.

Phenolic compounds have also been extracted from water samples using CNTs as stationary phases of SPME fibers [122,126,127,129] and also as sorbents for µ-SPE in packed as well as in an open tubular format [128], see Table 3. For these works, either MWCNTs [122,127–129] or SWCNTs [126,128] have been used, and analytes have been determined by HPLC-UV [122,126,128] and GC-FID [127,129]. Regarding the use of CNTs as stationary phases of SPME fibers, depositions have been carried out using electrophoretic deposition in metallic fibers [126,127], epoxy resin glue [122] or nafion [129]. As an example, Li et al. [126] prepared a novel SPME Pt fiber coated with SWCNTs by electrophoretic deposition with the aim of determining phenols, including phenol, *p*-nitrophenol, *m*-methylphenol, bisphenol A, 2-chlorophenol and 2,4-dichlorophenol, in sea and tap water by direct immersion SPME-HPLC-UV. Fig. 3 shows the SWCNTs deposit on the Pt wire. As it can be seen, two kinds of SPME fibers (*i.e.*, fiber A: 1 cm length, 25 µm thickness and 0.3 mm Pt wire diameter and fiber B: 1 cm length, 100 µm thickness and 0.1 mm Pt wire diameter) were electrophoretically prepared for 4 and 10 s of electrodeposition for fibers A and B, respectively. As a consequence, the amounts of SWCNTs coated on fibers A and B were only about 0.4 and 0.9 mg, respectively. The obtained results revealed that this kind of deposition was simple and reproducible technique for the preparation of SPME fibers coated with SWCNTs without the use of adhesives with mean recovery values between 88 and 102% and LODs in the range 0.9–3.8 µg/L.

Other compounds such as chlorobenzenes [131], polycyclic aromatic hydrocarbons (PAHs) [135], linear alkylbenzene sulfonates [137] and arginines, peptides and quinolinic alkaloids [132] have been extracted from water samples using CNTs-SPE prior to their determination by GC [131], HPLC [135,137] or MALDI-TOF [132]. For these works, non-functionalized MWCNTs [131,132,135] and functionalized MWCNTs [137] were employed. An example of the use of non-functionalized MWC-

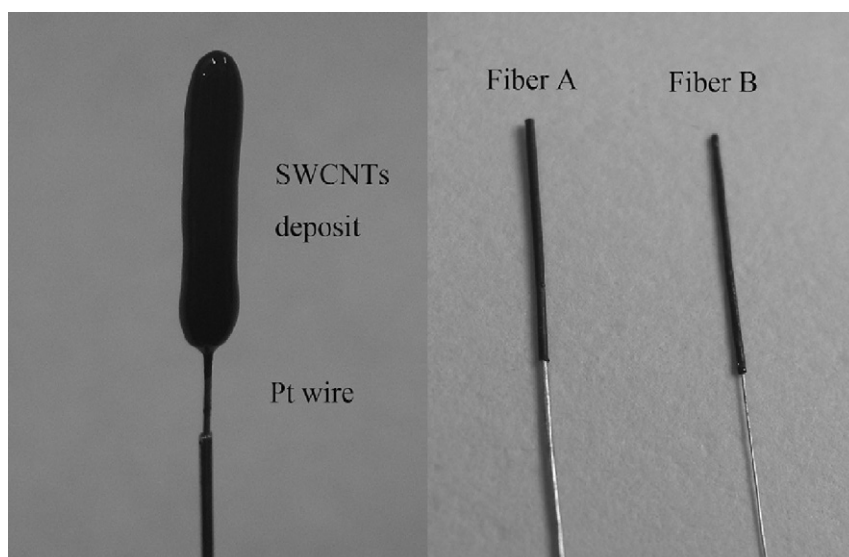


Fig. 3. Deposit of SWCNTs on Pt wire (left) and the prepared SPME fibers coated with SWCNTs (right). Fiber A: 1 cm length, 25 μm thickness, 0.3 mm Pt wire diameter and 4 s of electrophoretic deposition. Fiber B: 1 cm length, 100 μm thickness, 0.1 mm Pt wire diameter and 10 s of electrophoretic deposition. Reprinted from [126] with permission from Elsevier.

NTs as adsorbents in SPE is the work of Wang et al. [135], who developed a simple method to determine PAHs (*i.e.*, naphthalene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, benzo[*b*]fluoranthene and benzo[*k*]fluoranthene) in tap and river waters using MWCNTs of 30–50 nm (o.d.) in combination with HPLC-UV. After the optimization of the main parameters affecting the extraction efficiency, the sensitivity and precision of the method was investigated. LODs and recovery values achieved were in the range 5–58 ng/L and 79–117%, respectively. A comparison study between the behavior of MWCNTs and C_{18} was carried out, finding that the MWCNTs packed cartridge provided a more efficient performance. Concerning the use of functionalized MWCNTs, Guan et al. [137] investigated the use of carboxyl modified MWCNTs (CMMWCNTs) for the extraction of linear alkylbenzene sulfonates, including C_{10} , C_{11} , C_{12} and C_{13} , which are widely used anionic surfactants in large quantities. The good retention ability of CMMWCNTs for the analytes may be attributed to its high surface area and the presence of oxygen-containing functional groups such as $-\text{COOH}$, $-\text{OH}$ or $-\text{C}=\text{O}$. A comparison study with CMMWCNTs, C_8 and C_{18} revealed that CMMWCNTs cartridges showed stronger retention ability than C_8 or C_{18} cartridges for target compounds. Recovery values and LODs were in the range 85–106% and 20–30 ng/L, respectively. This work was the first application of CMMWCNTs as SPE adsorbents to pre-concentrate anionic surfactants.

Other groups of compounds have also been extracted using CNTs disposed in formats different from the conventional cartridge or disk. This is the case of CNTs stationary phases in SPME fibers [133,139,140,143], as sorbents for on-line SPE using a continuous flow system in which CNTs were into the sorbent column [134,141,142], for matrix solid-phase dispersion (MSPD) [138] and also for trapping volatile organic compounds [130]. As previously reported, a higher number of works have analyzed waters [130,133,138–141,143] and, in a much lower extent, other samples, like human blood [134,142], air [130] and milk [133]. Among these alternative techniques, the extraction by SPME fibers has been the most applied procedure. The different methods used to deposit the CNTs on the fiber include sol-gel fiber coating [140,143] and coating on the outer surface of a fused-silica tube or fiber [133,139]. Wang et al. [133] compared the extraction capacity of MWCNTs for polybrominated diphenyl ethers

(*i.e.*, 2,2',4,4'-tetraBDE, 2,2',4,4',5-pentaBDE, 2,2',4,4',6-pentaBDE, 2,2',4,4',5,5'-hexaBDE and 2,2',4,4',5,6'-hexaBDE) from river water, waste water and milk by using MWCNTs (coated fibers coating on the outer surface of a fused-silica tube or fiber), activated carbon and PDMS-DVB, finding that MWCNTs provided better results than classical stationary phases. Moreover, the obtained results revealed that no polybrominated diphenyl ethers were detected in river water and skimmed milk samples, whereas in waste water, whole fat milk and semiskimmed milk samples, residues of analytes were found. Another interesting work was developed by Liu et al. [139]. In this case, an automated on-line method which employed MWCNTs-COOH as in-tube SPME medium coupled to HPLC-UV was used for the determination of substituted aniline compounds, including 4-nitroaniline, 2-nitroaniline, 2-chloroaniline and 2,4-dichloroaniline. MWCNTs-COOH were coated on the outer surface of the fused-silica tube and inserted in a polyether ether ketone tubing which was fixed on the six-port injection valve of the HPLC instrument. After extraction in load position, the valve was switched to inject position and the elution was carried out by the mobile phase. High extraction capacity (56–110% recoveries) was achieved for the investigated analytes and great improvement of LODs (in the range 40–130 ng/L) was obtained in comparison with other methods.

2.2. Inorganic analytes

CNTs can also be utilized for the extraction of inorganic ions and organometallic compounds as it can be seen from the different articles compiled in Table 4. In these applications it is very important to indicate that apart from the previously indicated characteristics of CNTs, there exists a pH value called “point of zero charge” [144] or “isoelectric point”, at which CNTs surface has zero net charge. When pH is higher than the isoelectric point, the surface is negatively charged and thus electrostatic interactions can be established to adsorb cationic species. The presence of active sites on their surface, the inner cavities and inter-nanotube space contribute to the metal removal capability of CNTs. On the contrary, the decrease of pH below the point of zero charge, leads to its neutralization providing a decrease in the adsorption of cations [76,77,145]. Therefore, the effect of pH is crucial and should be carefully studied in SPE applications of CNTs for the extraction

Table 4
Applications of CNTs as SPE sorbents for the extraction of inorganic ions from different samples.

Analyte	Matrix	Method	CNTs characteristics	CNTs amount (mg)	Recovery (%)	LOD	Enrichment factor	Remarks	Reference
Cd ²⁺ , Mn ²⁺ and Ni ²⁺	Lake water	ICP-AES	MWCNTs: –	30	96–104	21–48 ng/L	25 (sample volume: 50 mL; reconstitution volume: 2 mL)	MWCNTs were reused before reflux with concentrated nitric acid for 1 h, washed with water until neutral pH and dried at 100 °C	[76]
Eu, Gd, Ho, La, Sm, Tb and Yb	Lake water and synthetic seawater	ICP-AES	MWCNTs: diameters: 15–55 nm	30	94–102	3–57 ng/L	50 (sample volume: 50 mL; reconstitution volume: 1 mL)	MWCNTs were reused before reflux with concentrated nitric acid for 1 h, washed with water until neutral pH and dried at 100 °C	[77]
Cu ²⁺	Lake and tap water	Flame AAS (FAAS)	MWCNTs: o.d.: 30–60 nm	50	96–102	0.42 µg/L	150 (sample volume: 150 mL; reconstitution volume: 1 mL)	MWCNTs were oxidized with concentrated nitric acid for 1 h in reflux before use	[145]
Trimethyllead (I), dimethyllead (II), triethyllead (I), diethyllead (II), methylmercury (I), ethylmercury (I), mercury (II), n-butyltin (III), di-n-butyltin (II), tri-n-butyltin (I) and tin (IV)	Water and coastal sediments	GC-MS	MWCNTs: o.d.: 2–15 nm, length: 1–10 µm	80	75–98	1–3 ng/L	83 (sample volume: 25 mL; reconstitution volume: 300 µL).	Fullerenes (C ₆₀ , C ₇₀), MWCNTs, graphitized carbon and RP-C ₁₈ were compared and the best results were provided by C ₆₀ , C ₇₀ and MWCNTs ANOVA test showed that there are no significant differences between C ₆₀ , C ₇₀ and MWCNTs	[146]
Cd ²⁺	Mineral, tap and river water, cigarette samples, and certified biological materials	FAAS	MWCNTs: i.d.: 10–40 nm, length: 5–20 µm	30	94–107	11.4 ng/L	51 (calculated as the ratio between the slopes of analytical curves with and without preconcentration)	Cigarette samples and biological materials were microwave digested. MWCNTs were used before reflux with concentrated nitric acid for 1 h at 120 °C	[147]
Cd ²⁺ , Pb ²⁺ , Cu ²⁺ , Zn ²⁺ and MnO ₄ ⁻	Tap, reservoir, and stream water	FAAS	MWCNTs: o.d.: 10–100 nm, length: 5–15 µm, 1–2 µm	200	81–100	8.7–378	20 (sample volume: 200 mL; reconstitution volume: 10 mL)	MWCNTs were dried at 80 °C before use. The work explored the effect of dimensions of MWCNTs on their efficiency towards metal ions. Cd was not recovered with the method. The best results were obtained with MWCNTs with o.d. of 10–30 nm and length of 5–15 µm	[73]
V ⁴⁺ and V ⁵⁺	Pond and tap water	Electrothermal AAS (ETAAS)	MWCNTs: average diameter: 9.5 nm, length: 1.5 µm	The MWCNTs filled a volume equivalent to 25 µL of water.	96–102	19 ng/L	20 (sample volume: 1 mL; reconstitution volume: 50 µL)	MWCNTs were dried overnight in a vacuum oven at 120 °C before use	[148]

Cd ²⁺	Snow and industrial wastewater	FAAS	MWCNTs: o.d.: 30–60 nm	200	91–108	0.15 µg/L	50 (sample volume: 250 mL; reconstitution volume: 5 mL)	MWCNTs were oxidized in a solution of potassium permanganate before use	[149]
Pb ²⁺	Tap, mineral and seawater, physiological serum, garlic, and Ginkgo Biloba	FAAS	–	30	90–96	2.6 µg/L	44.2 (calculated as the ratio between the slopes of analytical curves with and without preconcentration)	Garlic and ginkgo biloba were microwave digested. MWCNTs were oxidized with concentrated nitric acid for 1 h in reflux	[150]
Cr ³⁺ and Cr ⁶⁺	River water and waste water	FAAS	MWCNTs: o.d.: 30–50 nm, i.d.: 5–15 nm, length: 0.5–200 µm	300	95–98	0.90 µg/L	100 (sample volume: 500 mL; reconstitution volume: 5 mL)	–	[151]
Cu ²⁺	Ground, snow and river water	FAAS	MWCNTs: o.d.: 30–60 nm		90–111	0.32 µg/L	42 (sample volume: 250 mL; reconstitution volume: 6 mL)	MWCNTs were oxidized in a solution of potassium permanganate before use	[152]
Hg ²⁺	River, tap and lake water	Cold vapor-AFS	MWCNTs: o.d.: 40–60 nm, length 5–15 µm	6	90–96	1.2 ng/L	39 (sample volume: 6.6 mL; reconstitution volume: –)	–	[153]
Au ³⁺	Lake and seawater	FAAS	MWCNTs: o.d.: 30–60 nm	50	95–103	0.15 µg/L	75 (sample volume: 150 mL; reconstitution volume: 2 mL)	MWCNTs were reused before reflux with concentrated nitric acid for 1 h, washed with water until neutral pH and dried at 100 °C	[154]
Cu ²⁺	Pond water	FAAS	MWCNTs: o.d.: 5–10 nm	200	90–105	2.1 µg/L	50 (sample volume: 150 mL; reconstitution volume: 3 mL)	MWCNTs were soaked in HNO ₃ 8 M prior to use	[155]
Co ²⁺	Tap and river water	FAAS	MWCNTs: average diameter: 10–30 nm, length: 5–15 µm	40	98–100	0.55 µg/L	300 (sample volume: 900 mL; reconstitution volume: 3 mL)	MWCNTs were oxidized with HNO ₃ and modified with 1-(2-pyridylazo)-2-naphthol	[156]
Cu ²⁺ , Cd ²⁺ , Pb ²⁺ , Zn ²⁺ , Ni ²⁺ and Co ²⁺ as pyrrolidine dithiocarbamate chelates	Tap, spring, and seawater, tomato sauce, canned fish, apple leaves and chickpea	FAAS	MWCNTs: o.d.: 30–50 nm, i.d.: 5–15 nm, length: 0.5–200 µm	300	95–98	0.30–0.60 µg/L	80 (sample volume: 400 mL; reconstitution volume: 5 mL)	Biological samples were microwave digested	[157]
Cd ²⁺	Soil, polluted farmland soil, human hair, tea, and rice	FAAS	MWCNTs: average diameter: 40–60 nm, length: 1–2 µm	10	63–98	0.28 µg/L	33 (sample volume 5 mL; reconstitution volume: –)	On-line SPE. MWCNTs were suspended in a mixture of H ₂ SO ₄ :HNO ₃ 3:1, sonicated for 2 h and stirred at 55 °C for 7 h. MWCNTs were functionalized with L-Cysteine. Samples were microwave digested	[158]

Table 4 (Continued)

Analyte	Matrix	Method	CNTs characteristics	CNTs amount (mg)	Recovery (%)	LOD	Enrichment factor	Remarks	Reference
Co ²⁺ , Cd ²⁺ , Pb ²⁺ , Mn ²⁺ , Cr ³⁺ and Ni ²⁺ .	Tomato leaves, bovine liver, boiled wheat, canned fish, black tea, lichen and spring and tap water	FAAS	MWCNTs: o.d.: 30–50 nm, i.d.: 5–15 nm, length: 0.5–200 μm	250	95–102	0.24–2.60 μg/L	50 (sample volume: 500 mL; reconstitution volume: 10 mL)	Pseudomonas aeruginosa was immobilized onto MWCNTs. Samples were microwave digested	[159]
Cd ²⁺ , Cr ³⁺ , Pb ²⁺ , Zn ²⁺ , Cu ²⁺ and Mn ²⁺	Tap, reservoir, and stream water	FAAS	MWCNTs: o.d.: 10–30 nm, length 5–15 μm	200	–	9–378 ng/L	40 (sample volume: 400 mL; reconstitution volume: 10 mL)	Activated carbon (oxidized with HNO ₃ , H ₂ O ₂ and ammonium persulfate) was compared as extractor phase with MWCNTs oxidized and no oxidized. Oxidized MWCNTs provided similar results that activated carbon	[160]
H ₂ AsO ₄ [–]	River and tap water	Flow injection-AFS	MWCNTs: o.d.: 50 nm, length: 20 μm	200	94–104	2 ng/L	62.5 (sample volume: 500 mL; reconstitution volume: 8 mL)	Hemicelle capped carboxyl modified MWCNTs	[161]
Au ³⁺ and Mn ²⁺	Tap, well and waste water	FAAS	MWCNTs: length: 1–10 μm	40	94–102	0.01–0.03 μg/L	250 (sample volume: 1000 mL; reconstitution volume: 4 mL)	MWCNTs were oxidized with HNO ₃ and modified with N,N'-bis(2-hydroxybenzylidene)-2,2'-(aminophanylthio)ethane	[162]
Cu ²⁺	Tap and mineral water	FAAS	MWCNTs: o.d.: 20–40 nm, i.d.: 5–10 nm, length: 0.5–50 μm	200	98–99	1.46 μg/L	60 (sample volume: 600 mL; reconstitution volume: 10 mL)	–	[163]
Cu ²⁺ and Ni ²⁺	Certified reference materials: soils, tea leaf, human hair and tea	FAAS	MWCNTs: o.d.: 10–20 nm, length: 1–2 μm	15	81–100	0.31–0.63 μg/L	29 for Cu ²⁺ (sample volume: 78.3 mL; reconstitution volume: 2.7 mL) and 28 for Ni ²⁺ (sample volume: 75.6 mL; reconstitution volume: 2.7 mL)	MWCNTs were suspended in a mixture of H ₂ SO ₄ :HNO ₃ (3:1), sonicated for 2 h and stirred at 55 °C for 7 h. Hexahistidine-tagged protein functionalized MWCNTs. Samples were microwave digested	[164]
Cr ³⁺ , Fe ³⁺ and Pb ²⁺	River sediment, balsam pear leaves and water	ICP-OES	MWCNTs: o.d.: 15–65 nm, length: 10–50 μm	Dispersive: 20, column: 50	99–100	0.19–0.33 μg/L	200 (sample volume: 400 mL; reconstitution volume: 2 mL)	Dispersive and on column SPE. MWCNTs were refluxed with concentrated nitric acid for 12 h. Ethylenediamine-modified MWCNTs	[165]
Co ²⁺ , Cu ²⁺ , Ni ²⁺ , Pb ²⁺ , Fe ³⁺ and Mn ²⁺	River sediments and mineral and tap water.	FAAS	Double-WCNTs: o.d.: 5 nm, i.d.: 1.3–20 nm, length: 50 μm	200	80–100	0.5–6.9 μg/L	100 (sample volume: 500 mL, reconstitution volume: 5 mL)	–	[166]

Co ²⁺	Natural water.	FAAS	MWCNTs: –	10	101	50 ng/L	180 (sample volume: 10 mL; reconstitution volume: –)	On-line SPE. MWCNTs were treated with concentrated HNO ₃ . L-Tyrosine was immobilized MWCNTs. The retention capacity was compared to the divalent cations Cu ²⁺ , Ni ²⁺ and Zn ²⁺ and Co ²⁺ has the lower retention capacity onto MWCNTs	[167]
Cu ²⁺ , Co ²⁺ , Ni ²⁺ and Pb ²⁺ as o-cresolphthalein complexone chelates	River sediments, tap, sea spring and mineral water	FAAS	MWCNTs: o.d.: 20–40 nm, i.d.: 5–10 nm, length: 0.5–50 μm	200	95–102	1.64–5.68 μg/L	40 (sample volume: 400 mL; reconstitution volume: 10 mL)	–	[168]
Cu ²⁺ , Co ²⁺ and Pb ²⁺	Water and mussel	ICP-MS	SWCNTs: –	20	96–109	1.2–39 ng/L	50 (sample volume: 100 mL; reconstitution volume: 2 mL)	Samples were microwave digested. MWCNTs were refluxed in nitric acid at 140 °C for 1 h	[169]
Rh ³⁺ as 1-(2-pyridylazo)-2-naphthol complex	Tap, well, river, sea, and wastewater and platinum iridium alloy	FAAS	MWCNTs: o.d.: 3–20 nm, length: 1–10 μm	20	96–105	0.010 μg/L	120 (sample volume: 600 mL; reconstitution volume: 5 mL)	MWCNTs were refluxed with concentrated HNO ₃ for 6 h at 100 °C	[170]

–: Not indicated.

of metallic compounds [76,77,145–147,73,148–170]. In this sense, since metallic ions are poorly adsorbed at acidic pH, solutions containing HCl or HNO₃ are frequently used to promote ions elution [76,77,145,147,73,148–153,155–161,163,165–169].

Table 4 shows different examples of the use of CNTs for the SPE of metallic compounds previous to their analytical determination. As it can be seen, CNTs have been used to extract transition metals, mainly heavy metals, like ions [76,145,147,73,148–156,158–167,169,171] or chelates [157,168,170], rare earth elements [76,172], and organometallic compounds [146]. In these works the determination was made by atomic absorption spectrometry (AAS) [145,147,73,148–152,154–160,162–164,166–168,170], inductive coupled plasma-atomic emission spectrometry (ICP-AES) [76,77,165], atomic fluorescence spectrometry (AFS) [153,161], inductive coupled plasma-mass spectrometry (ICP-MS) [169–172] and gas chromatography–mass spectrometry (GC-MS) [146] (in the case of organometallic compounds). Experimental parameters (i.e., pH value, sample flow rate and volume, elution and interference effect of coexisting ions) were investigated in the great majority of works following a step by step approach.

After oxidation, CNTs have also shown exceptional adsorption efficiency for metal removal from waters [77,164,173]. Oxidized CNTs possess hydroxyl, carboxyl and carbonyl groups on their surface at its defect sites [173,175] and then metals are retained when the solution pH is higher than the isoelectric point of the oxidized CNTs. Thus, in many of these applications, CNTs are previously refluxed with nitric acid [76,77,145,147,150,154,162,165,170,173], or oxidized with either permanganate [149,152,171,173] or H₂O₂ [173]. Nitric acid treatment opens the end of MWCNTs, as can be seen in Fig. 4. MWCNTs are highly entangled by van der Waals forces to form a dense and robust network (Fig. 4a) while oxidized MWCNTs are relatively shorter (Fig. 4b).

Judging from the revision of the current literature, most research studies dealing with the extraction of inorganic compounds have generally used non-modified MWCNTs with amounts lower than 300 mg. Even though, recent works are using modified MWCNTs [156,158,159,161,162,164,165,167]. In this sense, Afzali and Mostafavi [156] modified MWCNTs with 1-(2-pyridylazo)-2-naphthol to determine Co(II) in water, since this reagent is a good complexing agent of Co(II). A solution of 1-(2-pyridylazo)-2-naphthol was added to MWCNTs and refluxed for 3 h at 75 °C. Its use allowed increasing the adsorption of Co from 65.6 to 99.7%. On the other hand, Li et al. [161] used a cationic surfactant (cetyltrimethylammonium chloride) to form hemimicelles with oxidized MWCNTs to extract H₂AsO₄[–] from river and tap water. The cationic alkylchain of the surfactant establishes electric interactions with negative functional groups on the surface of MWCNTs forming hemimicelle/admicelle aggregates. Although Cd(II), Mn(II), Ni(II), Cu(II), Co(II), Zn(II), and Pb(II) had been previously extracted by oxidized MWCNTs [76,145,73], the presence of these coexisting ions, which was also studied by the authors, does not make difficult the determination of arsenic because of the formation of hemimicelles, for which recoveries were higher than 94% for both types of waters. Another example is the work of Shamspur and Mostafavi [162] who determined Au(III) and Mn(II) in tap, well and waste water with MWCNTs previously modified with N,N'-bis(2-hydroxybenzylidene)-2,2'-(aminophanylthio)ethane. Preliminary experiments showed that MWCNTs retained both ions (62% for Mn(II) and 78% for Au(III)) but not selectively because other ions and organic materials can be adsorbed onto MWCNTs. Modified MWCNTs, however, allowed the selective determination of ions with higher recovery values (between 94 and 102%) and LODs values of 0.03 μg/L for gold and 0.01 μg/L for manganese. Liu et al. [164] used hexahistidine-tagged protein functionalized MWCNTs to extract Cu(II) and Ni(II) from soils, tea leaf, human hair and tea extracts after microwave digestion with concentrated HNO₃

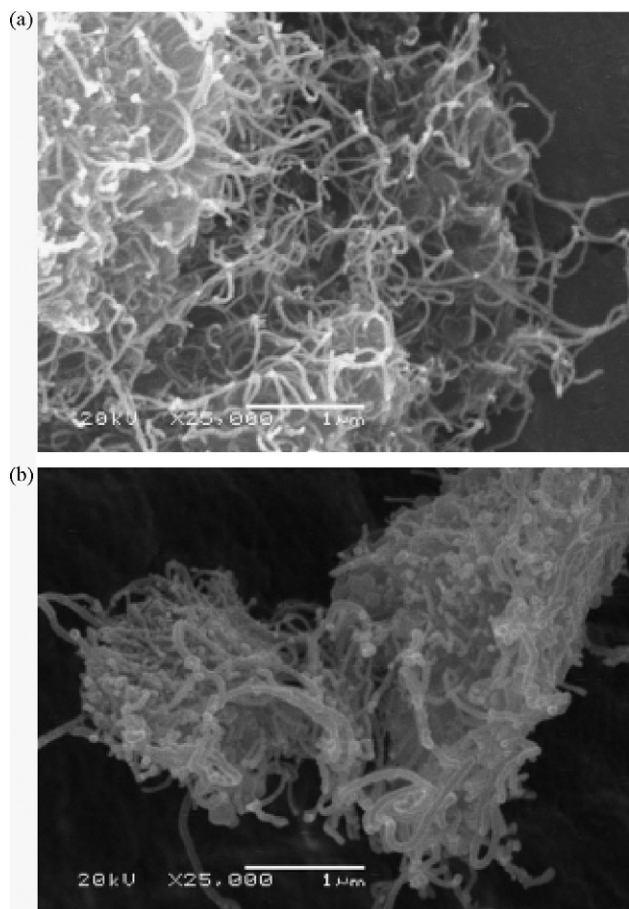


Fig. 4. Scanning electron micrographs of raw MWCNTs (a) and oxidized MWCNTs with concentrated HNO_3 (b). The images were amplified 25,000 times. Reprinted from [147] with permission from The Royal Society of Chemistry.

or H_2O_2 . Modified MWCNTs were characterized with UV–vis spectrometry and atomic force microscopy (AFM). These CNTs exhibited fast kinetics for the sorption of ions increasing up to 20,000 and 1800 times the tolerable concentration of coexisting ions over non-modified MWCNTs for SPE of $\text{Cu}(\text{II})$ and $\text{Ni}(\text{II})$. The presence of hexahistidine-tagged protein not only changed adsorption capacity but also modified the physical properties. As it can be observed in Fig. 5, morphology of the prepared MWCNTs shows globular structures on the wirelike MWCNTs. The region with hexahistidine-tagged protein shows a height of 19.9 nm while MWCNTs without protein have a height of 8.6 nm. Mean recovery values were in the range 81–100% with LODs of 0.31 $\mu\text{g/L}$ for $\text{Cu}(\text{II})$ and 0.63 $\mu\text{g/L}$ for $\text{Ni}(\text{II})$. The results demonstrated the selective extraction of Cu^{2+} and Ni^{2+} from complex matrices by these modified MWCNTs. Finally, Zhang et al. [165] applied ethylenediamine-modified MWCNTs for selective SPE of $\text{Cr}(\text{III})$, $\text{Fe}(\text{III})$ and $\text{Pb}(\text{II})$.

In most of the examples described in Table 4 aqueous samples were analyzed except in 14 cases where sediments [146,165,166,168], cigarettes [147], biological materials (serum, hair, animal tissues, etc.) [147,150,164], soils [158,164] and foods [150,157–159,164,169,171] were selected. Concerning sediments, Muñoz et al. [146] used 80 mg of MWCNTs (o.d. 2–15 nm) to extract organometallic compounds of lead, mercury and tin (trimethyllead (I), dimethyllead (II), triethyllead (I), diethyllead (II), methylmercury (I), ethylmercury (I), mercury (II), n-butyltin (III), di-n-butyltin (II), tri-n-butyltin (I) and tin (IV)) from water and coastal sediments. Sediments were first microwave digested with 5 mL of glacial acetic acid and 5 mL of 2 M HNO_3 for 3 min at 80 W. These compounds were complexed with diethyldithiocarbamate in a flow system and after preconcentration they were analyzed by GC–MS. The sorption capacity of MWCNTs, fullerenes, graphitized black carbon and C_{18} was compared. The results showed that MWCNTs and fullerenes were superior than other stationary phases for the extraction of the eleven compounds (no differences between them in terms of sensitivity, selectivity and precision were found). Recoveries were in the range 75–98%. Another example is the work of Zang et al. [165] who determined $\text{Cr}(\text{III})$, $\text{Fe}(\text{III})$ and $\text{Pb}(\text{II})$ in river sediments, balsam pear leaves and water by ICP optical emission spectrometry (ICP-OES)

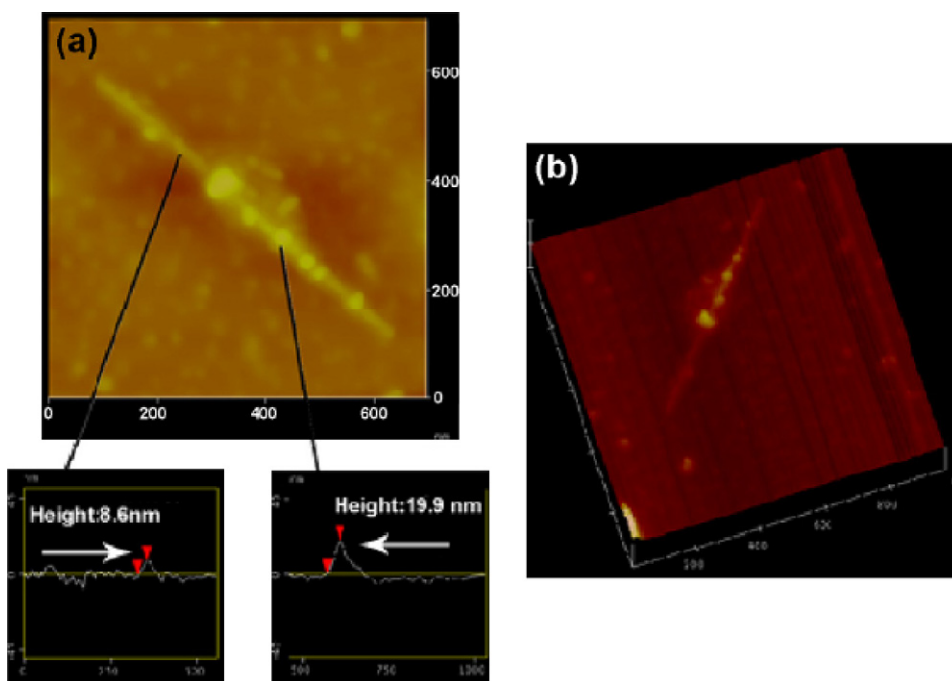


Fig. 5. Representative AFM images of (a) line scans with flattened images reveal MWCNTs/6His-tagged protein and (b) surface plot of height image for MWCNTs/6His-tagged protein. Reprinted from [164] with permission from Elsevier.

previously extracted by ethylenediamine-modified MWCNTs. Maximum adsorption capacity was found to be 39.58 mg/g for Cr(III), 28.69 mg/g for Fe(III) and 54.48 mg/g for Pb(II). Identification and characterization of surface modification was made by transmission electron microscopy, Fourier transform infrared and elemental analysis.

Regarding the analysis of foods and biological materials, eight works have used MWCNTs for the extraction of metals [147,150,171,157–159,164,169]. In all these cases samples were microwave digested in one or two steps with volumes of nitric acid between 6 and 10 mL (concentration in the range 65–100%) and volumes of H₂O₂ in the range 2–4 mL (concentrations between 30 and 100%) and later extracted by SPE. Teixeira-Tarley et al. [147] applied a flow preconcentration method for Cd determination in mineral, tap and river water, cigarette samples, rye grass and bovine liver obtaining a preconcentration factor of 51-fold. Experimental parameters were optimized by a fractional factorial design and response surface methodology which are more efficient and precise compared with the univariate method. The factors optimized in this work were pH, buffer concentration, preconcentration flow rate, eluent concentration and type of eluent. The significance of factors as well as interactions was checked by an ANOVA. The pH was the most important factor and its interaction with the buffer concentration was found to be highly significant. The obtained LOD (11.4 ng/L) and recoveries (in the range 94–107%) demonstrate that method can also be used to determine Cd²⁺ in biological materials with confidence. Results also demonstrated that the sorbent preconcentration system is not affected by potential interferences in different types of matrices. Barbosa et al. [150] investigated the effect of experimental parameters on the on-line extraction of Pb(II) from tap, mineral and seawater, physiological serum, garlic, and Ginkgo Biloba by means of a 2⁴ full factorial design and the final optimization was made by a Doehlert design (response surface methodology). Variables optimized in the study were pH, the preconcentration flow rate, buffer and eluent concentration. Other important variables such as mass of MWCNTs and flow rate of eluent were previously fixed. Under the best experimental conditions the SPE provided a LOD of 2.6 µg/L and recoveries between 90 and 96% with RSDs lower than 7%. Tuzen et al. [157] used MWCNTs for the extraction of heavy metals (Cu(II), Cd(II), Pb(II), Zn(II), Ni(II) and Co(II)) as ammonium pyrrolidine dithiocarbamate chelates in foods (tomato sauce, canned fish, apple leaves and chickpea) and environmental samples (tap, spring, and seawater). Food samples were previously microwave digested. Results obtained were similar to other works in the literature with a preconcentration factor of 80 and LODs in the range 0.30–0.60 µg/L (recoveries between 95 and 98%).

Some of the applications of MWCNTs have also been focused on the development of dispersive SPE procedures to study the adsorption capacity of this stationary phase [173,174,176–180]. For this purpose the amount of adsorbed metal is calculated as the difference between initial concentration and the concentration after the extraction, and experimental data is approximated by the isotherm models of Langmuir and/or Freundlich. An example is the work of Lu and Chiu [177] who studied the properties of MWCNTs of o.d. <10 nm and SWCNTs of o.d. <2 nm (both of them of the same length) and their adsorption capacity for the extraction of Zn(II) from water (50 mg were used in both cases). Besides, a comparative study between CNTs and powdered activated carbon demonstrated that SWCNTs and MWCNTs possess a higher capacity for the removal of Zn(II) from water. It was also noted that these SWCNTs have higher adsorption capacity for Zn(II) than MWCNTs because the surface area and pore volume available for liquid phase mass transfer are lower in MWCNTs, and the large number of defects present in MWCNTs may increase the electrical resistivity and decrease the adsorption of Zn(II) onto the surface. Later on, Lu et al. [178] extended

this work and investigated the kinetics and equilibrium of Zn(II) sorption by the same type of CNTs. They concluded that the sorption of Zn(II) is endothermic and spontaneous and that the sorption capacity is maintained after 10 cycles of sorption–desorption process. Li et al. [179] developed another work in which the kinetic and thermodynamics of adsorption of Pb(II) from water was studied. An interesting investigation was developed by Wang et al. [176] who analyzed the sorption capacity of Am(III) by MWCNTs. The effects of ion solution concentration, ionic strength, and pH were exhaustively studied. This group demonstrated the strongly dependence on pH values and the weakly dependence on the ionic strength. Chemosorption or chemicomplexation is the main sorption mechanism of Am(III) on the surface of MWCNTs.

3. Conclusions and future trends

CNTs have fascinated the scientific community since their discovery. These relatively new nanomaterials have found today a wide range of applications which also include the Analytical Chemistry area. In the search of new extraction materials, CNTs have found a growing application field in SPE procedures. Up to now, most of these applications have dealt with their use as stationary phases for the extraction of organic compounds (also using MSPD or SPME). A high number of these works have focused on pesticide extraction from water samples. As noted earlier, in most cases MWCNTs have been used.

From the study of the literature, it is clear that small quantities of CNTs (lower than those of conventional SPE cartridges) can be used as SPE materials and thus, they may play an important role in miniaturization of extraction procedures. In some cases, these materials are more expensive than conventional SPE cartridges, however, several works have also demonstrated that highly economic CNTs (with adequate SPE performance) are also available and thus they may also represent a good economic alternative.

At the present time, there are few applications of CNTs commercialized. This also occurs with SPE since no commercial cartridges, disks or SPME fibers are available, probably because of the relatively low number of works in this field (especially concerning SPME) and moreover, because their full potential in Analytical Chemistry has not yet been demonstrated. It is very likely that commercial CNTs-SPE cartridges will soon be available, but for this purpose CNTs should be fabricated at a larger scale. In this sense, it is important to develop efficient purification and characterization procedures to ensure the obtention of commercial, pure and well-characterized CNTs, in commercialized devices (cartridges, fibers, etc.) to promote the transmission of their use by laboratories. Besides, although studies have revealed that CNTs are not very toxic [181], their long-term impact on health should be studied in order to ensure a safe manipulation.

In recent years, work has progressed in getting different chemical varieties of CNTs which suggests a wide range of possible SPE materials (MWCNTs, SWCNTs, functionalized, non-functionalized, etc.) that have not been fully studied. As a result, a higher number of works, including the different chemical possibilities of CNTs are also expected as well as the application of CNTs in SPME devices.

Future developments on all these aspects will surely contribute to the extension of the use of CNTs as SPE materials in analytical science. Very probably, we will attend in a very near future to the appearance of many new and interesting publications on this attractive analytical field, especially concerning miniaturization.

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